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STUDY OF SPECIFIC SOLVATION EFFECTS ON THE REACTION KINETICS OF OLEFIN ALPHA OXIDES WITH HALIDE ANIONS. I.INTERACTION OF PHENYLGLYCIDYL ETHER WITH TETRAETHYLAMMONIUM CHLORIDE, TETRAETHYLAMMONIUM BROMIDE, AND TETRAETHYLAMMONIUM IODIDE.

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Received November 16, 1981

The reaction kinetics of phenylglycidyl ether with halide anions in propylene carbonate in the presence of proton-donating compound (phenol, ethanediol and butanol-1)has been studied.Specific solvation effects of reagents on the reaction rate are discussed. The relationship between acidity of proton-donating compounds and the rate constant as dependent on a reacting anion is reported.

A large body of literature is concerned with reaction kinetics of olefin alpha oxides.However,almost all the works are devoted to the interaction of oxides with various compounds in protic solvents,i.e.the interaction of solvated forms (due to formation of hydrogen bonds). On the basis of these works conclusions have been made about relative reactivity of various complexes of olefin oxides with hydroxyl containing compounds. It was impossible to estimate the reactivity of these complexes in comparison with unsolvated oxide.

In the present work such an attempt has been made.

The reaction of oxide with halide anions has been chosen as a model one. The choice is due to the possibility to carry out this reaction both in aprotic solvent (propylene carbonate) and under conditions of specific solvation of

reagents (solvent is a mixture of propylene carbonate with some proton-donating compound).

Reactants and Solvents

Phenylglycidyl ether ("Pure" grade) was redistilled under vacuum. Content of the main substance in the purified sample was not less than 99.5%.

Tetraethylammonium chloride, bromide and iodide ("Pure" grade) were used without additional purification. Content of the main substance was not less than 99.4%.

Propylene carbonate synthesized from the propylene oxide and carbon dioxide was dried over $CaCl_2$ and redistilled under vacuum. Water content in propylene carbonate (determined according to Fisher) was within 0.03% (by weight).

Phenol ("Pure" grade) was used without additional purification.

Ethanediol and 1-butanol were redistilled.

Experimental Technique

Reactivity of the olefin oxide-anion system was studied manometrically by the consumption of carbon dioxide as described in Ref. 1.

In this case, the reaction mixture involves the reaction which leads to the formation of cyclic carbonate.

$$C_3H_5OCH_2CH\text{-}CH_2 + Hal^- \rightleftharpoons C_6H_5OCH_2CH\text{-}CH_2Hal \quad (1)$$
$$\qquad\qquad\qquad

It was shown elsewhere by manometric technique that in propylene carbonate that the above reactions are irreversible and step (1) is the limiting step. Thus the experimental rate constant equals the reaction rate constant of the oxide with an anion i.e. the rate constant of the reaction of interest. To prove that the first step is the limiting one also when carrying out the reaction in the presence of proton-donating compounds the experiments were done by monitoring the instant concentration of an anion. The latter quantity equals, evidently, the initial one provided only that step (1) is the limiting one. Table 1 lists the results obtained.

Table 1

Values of the Instant Concentration of the Anion with Interaction of Phenylglycidyl Ether (PGE) with Chlorine, Bromine, and Iodine Anions in Propylene Carbonate (PC) Containing Proton-donating Additions.

$t = 109.6^{\circ}C$, initial concentrations:
PGE 0.520 $mol.l^{-1}$ ethanediol and butanol-1 0.750 $mol.l^{-1}$ and phenol 0.490 $mol.l^{-1}$.

t min	chlorine anion			bromine anion			iodine anion
	phenol	ethane-diol	1-bu-tanol	phenol	ethane-diol	1-bu-tanol	phenol
0	0.0417	0.0340	0.0360	0.0420	0.0406	0.0400	0.0420
20		0.0345		0.0407			
30	0.0274		0.0360	0.407			
60	0.0302	0.0340		0.0418	0.0402	0.0385	0.0415
110	0.0330	0.0343	0.0350		0.0410		0.0418
120				0.0396		0.0390	0.0414

Conversion of PGE for 110 min ranged from 36 to 80 per cent depending on the protic component and reacting anion.

From the Table one can see that step 1 is the limiting one with the exception of the reaction of PGE with the chlorine anion in the presence of phenol. In this case, either the

limiting step changes or the rates of all the steps become comparable.

Under experimental conditions the consumption of PGE which results from its interaction with a proton-donating compound can be neglected as the conversion degree of PGE in this direction ranges at most up to 10 per cent of the total conversion.

On the basis of the above and also taking into account the results of Ref.2, the interaction rate of phenylglycidyl ether with anions in propylene carbonate containing proton--donating impurities is described by the first order equation (4)

$$\frac{d/PGE/}{dt} = k_{exp.}/PGE/ \qquad (4)$$

Tables 2 and 3 list for example the values of k_{exp} of the reactions of PGE with anions in propylene carbonate depending on the conversion degree of PGE.

Table 2

Values of k_{exp} of the Reaction of PGE with Cl^- in PC Containing 0.760 $mol.l^{-1}$ of Ethanediol.

t,min	Conversion of PGE,%	k_{exp} 10^3,min^{-1}
28	15.0	5.80
50	24.8	5.75
88	40.0	5.80
	mean	5.78.

t^o= 109.6°C
Initial concentrations:
PGE 0.520 $mol.l^{-1}$
$(C_2H_5)_4NCl$ 0.0416 $mol.l^{-1}$

Table 3

Values of k_{exp} of the Reaction of PGE with Br^- in PC Containing 0.246 $mol.l^{-1}$ of Phenol

t,min	Conversion of PGE,%	$k_{exp.}$ 10^3,min^{-1}
7	15.8	24.7
10	22.1	25.4
20	39.0	24.8
	mean	25.0

t^o= 109.6°C
Initial concentrations:
PGE 0.520 $mol.l^{-1}$
$(C_2H_5)_4NBr$ 0.0428 $mol.l^{-1}$

Tables 4-6 and Figs. 1-3 represent the plots of the reaction rate constants of PGE with anions vs. concentration of proton-donating substance in propylene carbonate. The complicated nature of these dependences is due to the following.

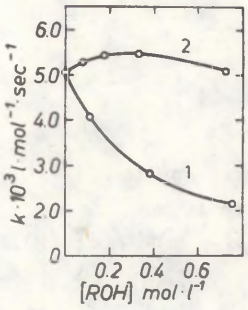

Fig.1. Plot of the reaction rate constants of PGE with the chlorine anion in PC vs. concentration of ethanediol (1) and 1-butanol (2) at 109.6°C. Initial concentrations:
PGE 0.520 mol.l^{-1}
$(C_2H_5)_4NCl$ 0.0420 ÷ 0.0460 mol.l^{-1}

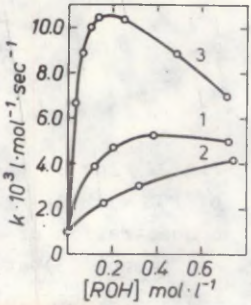

Fig.2. Plot of the reaction rate constant of PGE with the bromine anion in PC vs. concentration of ethanediol(1), 1-butanol(2), and phenol(3) at 109.6°C. Initial concentrations: PGE 0.520 mol.l^{-1}
$(C_2H_5)_4NBr$ 0.0410 ÷ 0.0425 mol.l^{-1}

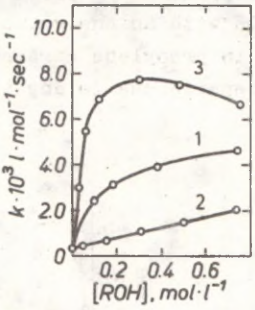

Fig.3. Plot of the reaction rate constant of PGE with the iodine anion in PC vs. concentration of ethanediol (1), 1-butanol (2), and phenol (3) at 109.6°C.
Initial concentrations:
PGE 0.520 mol.l^{-1},
$(C_2H_5)NI$ 0.0420 ÷ 0.0455 mol.l^{-1}

When adding proton-donating compounds to aprotic propylene carbonate, specific solvation of reagents (phenylglycidyl ether and anion) takes place. Olefin oxide (complex B) solvated at the expense of the hydrogen bond formations is known[3] to be more reactive than the unsolvated form due to the weakening of the oxide cycle C-O bond. On the other hand, solvation of an anion leads to the decrease in its nucleophilic activity.

$$C_6H_5OCH_2CH\text{-}CH_2 \;(O) + ROH \overset{K_p}{\rightleftharpoons} \underset{(B)}{C_6H_5OCH_2CH\text{-}CH_2\;(O)\cdots H\text{-}OR} \qquad (5)$$

The manifestation of the two effects specifies the nature of the dependence of the rate constant on the concentration of the proton-donating compound in propylene carbonate. One would assume that solvation of the chlorine anion makes the largest contribution and that of the iodine anion the least one to the

over-all effect.

This assumption is confirmed by the plots obtained (Figs 1-3). Thus reactions of phenyl-glycidyl ether with bromine anions are accelerated with adding proton-donating compounds (ethanediol and butanol-1) over the whole range of their concentrations studied and phenol in the concentration range from 0 to 0.2 $mol.l^{-1}$ to aprotic propylene carbonate .

Activating effect of the proton-donating compound is manifested to a greater extent with interaction of phenyl-glycidyl ether with iodine anion. Hence, for these reactions, in the range of low concentrations of proton-donating compounds the main effect on changes in the rate constant is exerted by specific solvation of phenylglycidyl ether. The rate constant increases with increase in the acidity of protic addition.

Another picture is observed when phenylglycidyl ether interacts with the chlorine anion. In this case, solvation of the anion plays a major role and leads to a decrease in the reaction rate with an increase in the proton-donating compound concentration. Increase in the acidity of the latter results in the decrease in the rate constant.

Table 4.

Reaction Rate Constants of Phenylglycidyl Ether with Tetraethylammonium Chloride in Propylene Carbonate at $109.7\pm0.1^{\circ}C$ at Various Concentrations of the Proton-donating Compound. k $l.mol^{-1}.sec^{-1}$

/ethanediol/ $mol.l^{-1}$	0	0.109	0.380	0.755
$k.10^3$	5.0 ± 0.2	4.2 ± 0.2	2.8 ± 0.15	2.2 ± 0.15

/1-butanol/ $mol.l^{-1}$	0	0.0815	0.176	0.329	0.720
$k.10^3$	5.0 ± 0.2	5.3 ± 0.2	5.5 ± 0.2	5.5 ± 0.2	5.1 ± 0.2

Table 5

Reaction Rate Constants of Phenylglycidyl Ether with Tetraethylammonium Bromide in Propylene Carbonate at 109.7±0.1°C at Various Concentrations of the Proton-donating Compound. k l.mol.$^{-1}$.sec^{-1}

/ethanediol/ mol.l^{-1}	0	0.118	0.198	0.380	0.722
k.10^3	0.95±0.03	3.9±0.2	4.7±0.2	5.2±0.2	5.0±0.2

/1-butanol/ mol.l^{-1}	0	0.157	0.312	0.748
k.10^3	0.95±0.03	2.3±0.15	3.0±0.15	4.2±0.2

/phenol/ mol.l^{-1}	0.0327	0.0625	0.0940	0.131	0.246	0.485	0.705
k.10^3	6.7±0.3	8.9±0.3	10.0±0.4	10.5±0.4	10.4±0.4	8.9±0.3	7.0±0.3

Table 6

Reaction Rate Constants of Phenylglycidyl Ether with Tetraethylammonium Iodide in Propylene Carbonate at 109.7±0.1°C at Various Concentrations of the Proton-donating Compound k l.mol.$^{-1}$sec^{-1}

/ethanediol/ mol.l^{-1}	0	0.100	0.185	0.382	0.742
k.10^3	0.36±0.02	2.4±0.1	3.1±0.2	3.9±0.2	4.7±0.2

/1-butanol/ mol.l^{-1}	0.050	0.156	0.308	0.500	0.746
k.10^3	0.45±0.02	0.68±0.04	1.1±0.05	1.5±0.1	2.1±0.1

Table 6 (continued)

/phenol/ mol.l^{-1}	0.030	0.062	0.124	0.300	0.483	0.750
k.10^3	3.0±0.15	5.5±0.2	6.9±0.4	7.8±0.4	7.6±0.4	6.7±0.4

$$k = \frac{k_{exp}}{/anion/}$$

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STUDY OF SPECIFIC SOLVATION EFFECT ON THE REACTION KINETICS OF OLEFIN ALPHA OXIDES WITH HALIDE ANIONS. 2. INTERACTION OF ALLYLGLYCIDYL ETHER AND EPICHLOROHYDRIN WITH TETRAETHYLAMMONIUM CHLORIDE, TETRAETHYLAMMONIUM BROMIDE, AND TETRAETHYLAMMONIUM IODIDE.

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The reaction kinetics of allylglycidyl ether and epichlorohydrin with halide anions in propylene carbonate in the presence of proton-donating compound (mono and dibasic alcohols and phenol) has been studied

Effects of the oxide structure and acidity of proton-donating compounds and the reacting anion on the olefin oxide-anion system reactivity are discussed.

The present work continues the study of specific solvation effects on the olefin oxide-anion system[1]. It deals with the reaction kinetics of allylglycidyl ether and epichlorohydrin with halide anions in aprotic propylene carbonate containing additions of various proton-donating com - pounds.

Experimental technique and purification of reagents and solvents are described in detail in Ref.1. However, this technique cannot be used in the case of interaction of allylglycidyl ether (AGE) and epichlorohydrin (ECH) with the chlorine anion in propylene carbonate in the presence of phenol.

The experimental technique provides the constant concentration of the anion in the solution (the concentration equals the initial one) and. hence, the experimental rate constant is calculated by the first order equation. The rate constants in Tables 1-6 and the Figs. are quotients of experimental constants by the reacting anion concentration.

Nature of the regularities studied depends on the contribution of the specific solvation of the olefine oxide (accelerates the reaction rate) and anion(decelerates the interaction) to the over-all solvation effect. The analysis of the dependences in Figs. 1-3 enables us to conclude that in the case of interaction of ECH with the chloride anion the main contribution to the over-all solvation effect is made up by the specific solvation of the anion. The rate constant decreases with a decrease in the acidity of proton--donating compounds. In the olefin oxide-iodide anion system the main effect on the interaction rate is exerted by the oxide solvation. An intermediate result is obtained for the reaction of ECH.

Table 1

Reaction Rate Constants of Allylglycidyl Ether with Tetraethylammonium Chloride in Propylene Carbonate at $130.2\pm0.1^{\circ}C$ at Various Concentrations of the Proton--donating Compound Added k $1.mol^{-1}.\ sec^{-1}$

/ethanediol/ $mol.l^{-1}$	0	0.975	0.193	0.300	0.384	0.750
$k\ .\ 10^3$	5.3 ± 0.3	5.7 ± 0.3	5.4 ± 0.3	4.5 ± 0.2	3.8 ± 0.2	2.1 ± 0.1

/butanol-1/ $mol.l^{-1}$	0.0820	0.200	0.318	0.500	0.616	0.750
$k.\ 10^3$	5.7 ± 0.3	6.3 ± 0.4	6.8 ± 0.4	6.9 ± 0.4	6.7 ± 0.4	6.4 ± 0.4

Table 2.

Reaction Rate Constants of Allylglycidyl Ether with Tetraethylammonium Bromide in Propylene Carbonate at 130.2±0.1°C at Various Concentrations of the Proton-donating Compound Added k $l.mol.^{-1}sec^{-1}$

/1-butanol/ $mol.l^{-1}$	0	0.161	0.318	0.616	0.750
$k.10^3$	0.82±0.05	1.5±0.1	2.1±0.1	2.8±0.15	3.1±2

/ethanediol/ $mol.l^{-1}$	0.0975	0.193	0.420	0.500	0.750
$k.10^3$	4.2±0.2	5.1±0.2	5.9±0.3	5.1±0.3	5.9±0.3

/phenol/ $mol.l^{-1}$	0.0644	0.127	0.247	0.350	0.493	0.740
$k.10^3$	10.2±0.6	11.5±0.7	11.1±0.7	10.0±0.6	7.9±0.4	6.7±0.5

Table 3

Reaction Rate Constants of Allylglycidyl Ether with Tetraethylammonium Iodide in Propylene Carbonate at 130.2±0.1°C at Various Concentrations of the Proton-donating Compound Added k $l.mol.^{-1}.\ sec^{-1}$

/1-butanol/ $mol.\ l^{-1}$	0	0.176	0.319	0.616	0.750
$k.10^3$	0.26±0.01	0.60±0.04	0.81±0.05	1.05±0.06	1.10±0.06

/ethanediol/ $mol.l^{-1}$	0.0975	0.193	0.384	0.750
$k.10^3$	2.3±0.1	2.8±0.1	3.2±0.2	3.5±0.2

/phenol/ $mol.l^{-1}$						
$k.10^3$	4.0±0.2	6.5±0.3	7.2±0.4	7.5±0.4	7.3±0.4	6.5±0.3

Table 4.

Reaction Rate Constants of Epichlorohydrin with Tetraethylammonium Chloride in Propylene Carbonate at 90.0±0.1°C at Various Concentrations of the Proton-donating Compound Added. k $l.mol^{-1}$ sec^{-1}

/1-butanol/ $mol.l^{-1}$	0	0.161	0.318	0.616	0.760
$k.10^3$	4.5±0.2	4.3±0.2	4.1±0.2	3.7±0.2	3.6±0.2

/ethanediol/ $mol.l^{-1}$	0.0485	0.0975	0.193	0.384	0.746
$k.10^3$	3.5±0.2	2.80±0.1	2.4±0.1	1.7±0.1	1.3±0.1

/propandiol-1,2/ $mol.l^{-1}$	0.0795	0.159	0.310	0.605	0.750
$k.10^3$	3.1±0.2	2.60±0.1	2.1±0.1	1.6±0.1	1.4±0.1

/1-propanol/ $mol.l^{-1}$	0.0905	0.198	0.394	0.760
$k.10^3$	4.3±0.2	4.1±0.2	3.7±0.2	3.3±0.2

/2-propanol/ $mol.l^{-1}$	0.200	0.394	0.550	0.760
$k.10^3$	4.3±0.2	4.1±0.2	4.0±0.2	3.9±0.2

Table 5

Reaction Rate Constants of Epichlorohydrin with Tetraethylammonium Bromide at Various Concentrations of the Proton-donating Compound k $l.mol^{-1}.sec^{-1}$

/1-butanol/ $mol.l^{-1}$	0	0.0820	0.161	0.318	0.616	0.750
$k.10^3$	1.97±0.08	2.5±0.1	2.7±0.1	3.1±0.1	3.6±0.1	3.7±0.1

Table 5 (continued)

/ethanediol/ mol.l^{-1}	0.0485	0.0975	0.193	0.384	0.746
k.10^3	2.6±0.1	3.0±0.1	3.2±0.1	3.0±0.1	2.5±0.1

/propandiol-1,2/ mol.l^{-1}	0.0795	0.159	0.310	0.605	0.750
k.10^3	2.9±0.1	3.1±0.1	3.3±0.1	3.3±0.1	3.2±0.1

/phenol/ mol.l^{-1}	0.0322	0.0644	0.127	0.247	0.493	0.750
k.10^3	4.4±0.2	5.3±0.2	5.6±0.2	5.5±0.2	3.9±0.1	3.3±0.1

/alcohol/ mol.l^{-1}	0.101	0.198	0.394	0.760
k.10^3 (1-propanol)	2.7±0.1	3.1±0.1	3.5±0.1	3.8±0.1
k.10^3 (2-propanol)	2.4±0.1	2.7±0.1	3.1±0.1	3.5±0.1

Table 6

Reaction Rate Constants of Epichlorohydrin with Tetraethylammonium Iodide in Propylene Carbonate at 90.0±0.1°C at Various Concentrations of the Proton-donating Compound

k l.mol^{-1}. sec^{-1}

/1-butanol/ mol.l^{-1}	0	0.0815	0.161	0.318	0.750
k.10^3	0.85±0.03	1.20±0.05	1.48±0.05	1.84±0.07	2.3±0.1

/ethanediol/ mol.l^{-1}	0.0485	0.0975	0.193	0.384	0.746
k.10^3	1.60±0.06	1.87±0.07	2.15±0.09	2.32±0.09	2.4±0.1

/propandiol-1,2/ mol.l^{-1}	0.0795	0.159	0.310	0.750
k.10^3	1.95±0.08	2.26±0.09	2.4±0.1	2.5±0.1

Table 6 (continued)

/phenol/ $mol.l^{-1}$	0.0644	0.120	0.247	0.493	0.750
$k.10^3$	3.0 ± 0.1	3.4 ± 0.1	3.5 ± 0.1	3.5 ± 0.1	3.1 ± 0.1

/2-propanol/ $mol.l^{-1}$	0.107	0.208	0.408	0.760
$k.10^3$	1.16 ± 0.04	1.42 ± 0.06	1.70 ± 0.07	2.01 ± 0.08

/1-propanol/ $mol.l^{-1}$	0.198	0.405	0.760
$k.10^3$	1.45 ± 0.06	1.88 ± 0.07	2.18 ± 0.09

$$k = \frac{k_{exp}}{/\ anion\ /}$$

with the bromine anion, the relationship between the acidity of a proton-donating compound and the rate constant value depending to a great extent on the proton donor concentration.

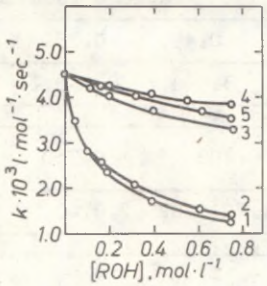

Fig.1. Plot of the reaction rate constant of epichlorohydrin with the chlorine anion in propylene carbonate vs. concentration of ethanediol (1), propandiol-1,2(2), 1-propanol (3), 2-propanol (4) and 1-butanol (5) at 90°C

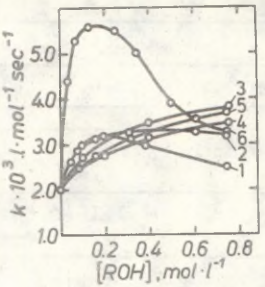

Fig.2. Plot of the reaction rate constant of epichlorohydrin with the bromine anion in propylene carbonate vs. concentration of ethanediol (1), propandiol-1,2 (2), 1-propanol (3), 2-propanol (4), 1-butanol (5), and phenol (6) at 90.0°C.

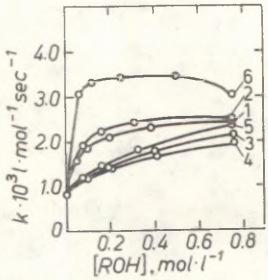

Fig.3. Plot of the reaction rate constant of epichlorohydrin with the iodine anion in propylene carbonate vs. concentration of ethanediol (1), propandiol-1,2(2), 1-propanol (3), 2-propanol (4), 1-butanol (5), and phenol (6) at 90.0°C.

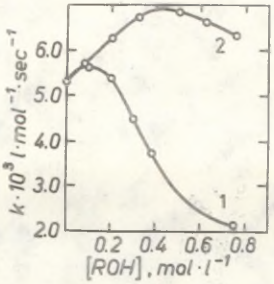

Fig.4. Plot of the reaction rate constant of allylglycidyl ether with the chlorine anion in propylene carbonate vs. concentration of ethanediol (1) and 1-butanol (2) at 130.2°C.

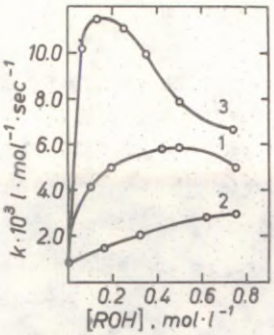

Fig.5. Plot of the reaction rate constant of allylglycidyl ether with the bromine anion in propylene carbonate vs. concentration of ethanediol (1), 1-butanol (2), and phenol (3) at 130.2°C.

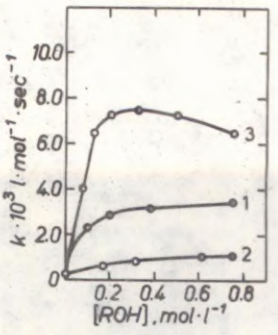

Fig.6. Plot of the reaction rate constant of allylglycidyl ether with the iodine anion in propylene carbonate vs. concentration of ethanediol (1), 1-butanol (2), and phenol (3) at 130.2°C.

The reaction of allylglycidyl ether with anions is also very sensitive to the reagent specific solvation. A characteristic feature of this reaction by comparison with that of epichlorohydrin is the significantly greater contribution of the AGE solvation to the total solvation effect of reagent.

The experimental data obtained in this work and also in Ref.1. will evidently allow to calculate the reactivities of solvated and unsolvated reagent forms in the interaction studied.

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STUDY OF S_N1 REACTIONS USING TRIPHENYLVERDAZYLIS. VI. KINETICS AND MECHANISM OF Ph_2CHBr IONIZATION IN NITROBENZENE AND ACETONE. NATURE OF SALT EFFECTS DURING HETEROLYSIS OF BENZHYDRYL DERIVATIVES

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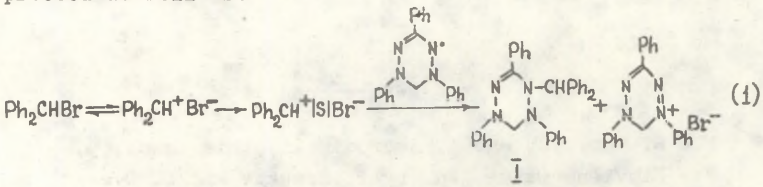
The Ph_2CHBr heterolysis rate in $PhNO_2$ and Me_2CO in the presence of triphenylverdazyl, used as the internal indicator, is described by the equation $v = k[Ph_2CHBr]$. In $PhNO_2$ in the presence of Et_4NClO_4 additions the special salt effect is observed. In acetone Et_4NClO_4 has no effect on the reaction rate, $LiClO_4$ additions increase the rate, where as those of LiCl lead to a decrease of the latter. Additions of dibenzo-18-crown-6 do not influence the Ph_2CHBr heterolysis rate in CH_3CN either in the presence of salts ($LiClO_4$, LiBr) or without them. Conversion of the intimate ion pair into the solvent-separated one is supposed to occur at the rate-determining step of the reaction. A generalized scheme of salt effects in the discussed process is given.

The reaction of Ph_2CHBr with triphenylverdazyl in MeCN, PhCN and 1,2-dichlorethane solutions has been shown earlier to proceed as follows:



(1)

At the rate-determining stage the intimate ion pair (IIP) of the substrate is converted into the solvent-separated ion pair (SSIP) the latter forming substituted tetrazine I and triphenylverdazylium bromide (Vd^+Br^-) in the rapid reaction with Vd•. The reaction rate is unaffected bv Vd• con-

centration and is described by the first-order kinetic equation

$$-d[Vd^{\cdot}]/2dt = d[Vd^{+}Br^{-}]/dt = k[Ph_2CHBr] \qquad (2)$$

As a further step in the study of solvent effect on the kinetic parameters of the above reaction the kinetics of Ph_2CHBr heterolysis in acetone and $PhNO_2$ was studied in the presence of $Vd^{\cdot}$ as the internal indicator. In both solvents the reaction rate is fairly well described by equation (2). Conditions and results of kinetic runs are given in Tables 1 and 2.

Table 1

Kinetics of Ph_2CHBr Ionization in $PhNO_2$ in the Presence of $Vd^{\cdot}$

Nos	$[Ph_2CHBr]\cdot10^2$M	$[Vd^{\cdot}]\cdot10^4$M	°C	$10^8k^{a)}$, s^{-1}	$10^8k_{av.}$, s^{-1}
1	6.77	1.38	25.0	4.21	4.13±0.08
2	8.69	1.38		4.04	
3	6.33	1.27	30.0	6.50	6.59±0.09
4	7.02	1.27		6.67	
5	6.13	1.35	35.5	11.9	11.0±1.0
6	3.06	1.35		10.0	
7	6.04	1.40	37.5	13.4	13.5±0.1
8	6.75	1.40		13.6	
9	5.83	1.73	43.1	19.2	19.6±0.4
10	5.83	0.864		20.0	
11[b)]	6.11	1.27		5.40	
12[c)]	6.11	1.27		5.46	
13[d)]	6.20	1.27	25.0	5.78	
14[e)]	5.95	1.29		6.00	
15[f)]	6.24	1.29		6.47	

a) Average of two determinations by the consumption of $Vd^{\cdot}$

b) In the presence of $0.41\cdot10^{-2}$M Et_4NClO_4

c) In the presence of $0.61\cdot10^{-2}$M Et_4NClO_4

d) In the presence of $1.23\cdot10^{-2}$M Et_4NClO_4

e) In the presence of $1.50\cdot10^{-2}$M Et_4NClO_4

f) In the presence of $2.50\cdot10^{-2}$M Et_4NClO_4

Et_4NClO_4 additions in $PhNO_2$ solution increase the reaction rate (Table 1, runs 11-15) and the special salt effect is observed (Fig., (a). The above suggests SSIP formation in the substrate[2,5]. The first section of the curve shows intermediate formation with perchlorate participation, whereas the second refers to the usual salt effect. The extrapolation of the last curve section to $[Et_4NClO_4] = 0$ gives the maximum value of the special salt effect in the absence of the usual salt effect, $k_s^o = 5.1 \cdot 10^{-8} s^{-1}$, i.e. the value being 1.2 times greater than that of the rate constant without salt additions. The latter means[2] that the ion triplet ($ClO_4^- | s | Ph_2CH^+Br^-$) or quadrupole ($Ph_2CH^+Br^-$, $Et_4N^+ClO_4^-$) forming under the action of ClO_4^- (Et_4NClO_4) on the IIP is converted into SSIP 1.2 times quicker as compared th the non-catalysed reaction $Ph_2CH^+Br^- \rightarrow Ph_2CH^+ | s | Br^-$.

"b" value in Winstein's equation

$$k_s = k_s^o (1 + b[Et_4NClO_4]) \qquad (3)$$

for the second section of the curve is 11 (the usual salt effect, reflecting the effect of Et_4NClO_4 concentration on the rate of ion triplet (or quadrupole) conversion into SSIP). In MeCN (ε 37.5, Z 71.3) which is noticeably more polar than $PhNO_2$ (ε 34.5, Z 66.3), Ph_2CHBr heterolysis rate is app. 1.5 orders higher ($\lg k^{25} = -5.6$)[1]. In this solvent Et_4NClO_4 also shows the special salt effect with the parameters ($k_s^o/k = 1.2$, $b = 8$, 25^oC)[2] being approximately the same as in $PhNO_2$. In less polar PhCN (ε 25.2, Z 65.0) and dichlorethane (ε 11.0, Z 63.5) the special salt effect of Et_4NClO_4 is more evident (in PhCN $k_s^o/k = 2.0$, $b = 46$ (40.5^oC)[3]; in dichlorethane $k_s^o/k = 2.5$, $b = 21$*) (40.5^o)[4]. This is conspicucus both for the special[5] and usual salt effects[6] - these are more pronounced in low polarity solvents. In the transition from Et_4NClO_4 to $LiClO_4$ special and usual salt effects acquire greater intensity, in MeCN $k_s^o/k = 1.3$, $b = 22$; in PhCN $k_s^o/k = 7.0$, $b = 210$. In acetone (ε 20.5, Z 65.7), the polarity of which is close to that of PhCN and noticeably lower

*) calculated using Fig. 2 of ref. 4

than those of $PhNO_2$ and MeCN, the additions of Et_4NClO_4 have practically no effect on the reaction rate (Table 2, runs 14,15;Fig.,(b)),whereas the addition of $LiClO_4$ enhances the reaction rate, however,no special salt effect is observed (Table 2, runs 11-13,Fig. (b)).

Since in MeCN,$PhNO_2$,PhCN and dichloroethane the special salt effect of perchlorate was observed and the absence of the mass action salt effects[2] (no carbocation is formed) was shown in the most polar of the above solvents (MeCN) it seems quite reasonable to suggest the conversion of IIP into SSIP in the above listed solvents at the rate-determining step of Ph_2CHBr heterolysis. The same is relevent to

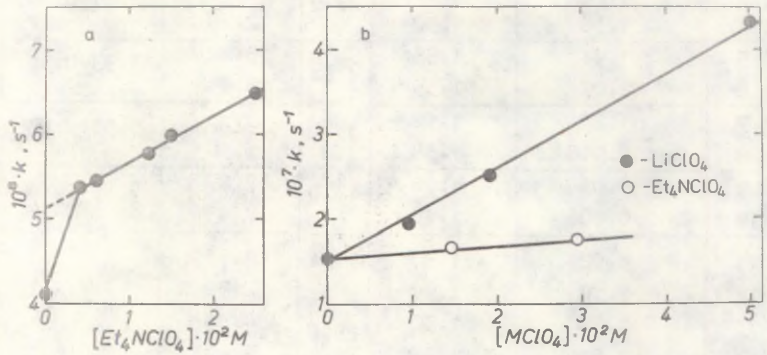


Fig. Perchlorate effect on the heterolysis rate of Ph_2CHBr in $PhNO_2$ (a) and acetone (b)

acetone which has a medium polarity value in the shown group of solvents. In all these cases triphenylverdazyl manifests itself as a SSIP indicator. An additional confirmation is the negative salt effect of LiCl in the presence of verdazyl (Table 2, run 16) due to a decrease in the SSIP formation rate[2]. Thus, the absence of the special salt effect cannot be an argument against intermediate SSIP formation.

Apart from our papers the special salt effect for benzhydryl systems has been reported earlier in the anion exchange reaction in 4,4'-dimethyl diphenylmethyl thiocianate in Me_2CO ($NaClO_4$ action)[7], in the solvolysis of benzhydryl-n-nitro-benzoate in aqueous acetone (NaN_3, Bu_4NN_3)[8] and in the hydrolysis of Ph_2CHCl and n-chlorbenzhydryl chloride in 80% acetone ($Co(NO_3)_2$)[9].

Table 2

Kinetics of Ph_2CHBr Ionization in Acetone in the Presence of Vd°

Nos.	$[Ph_2CHBr]\cdot10^2$M	$[Vd^\circ]\cdot10^4$M	°C	$10^7k^{a)}$, s^{-1}	$10^7k_{av.}$, s^{-1}
1	4.13	1.13	24.6	1.55	1.55±0.01
2	4.13	2.25		1.54	
3	2.72	1.30	29.5	2.13	2.21±0.08
4	1.36	1.30		2.29	
5	1.94	1.55	34.0	3.22	3.33±0.11
6	2.07	1.55		3.44	
7	1.26	1.12	39.0	5.55	5.53±0.03
8	0.948	1.38		5.50	
9	1.03	1.16	43.0	7.27	7.35±0.08
10	0.806	1.16		7.43	
11[b)]	3.92	1.90	25.0	1.93	
12[c)]	2.10	1.90		2.52	
13[d)]	1.96	1.30		4.36	
14[e)]	2.93	1.53		1.67	
15[f)]	2.93	1.53		1.75	
16[g)]	4.12	1.75		0.681	

a) Average of two determinations by the consumption of Vd°
b) In the presence of $0.95\cdot10^{-2}$M $LiClO_4$
c) In the presence of $1.90\cdot10^{-2}$M $LiClO_4$
d) In the presence of $5.02\cdot10^{-2}$M $LiClO_4$
e) In the presence of $1.46\cdot10^{-2}$M Et_4NClO_4
f) In the presence of $2.91\cdot10^{-2}$M Et_4NClO_4
g) In the presence of $1.63\cdot10^{-2}$M LiCl

In the first two cases where the effect is determined by the anion action it is rather vague. In the latter case the ef-

fect is connected with the cation action which falls out of the framework of Winstein's interpretation. Leffek[10] and Gordon[11] regard Winstein's[12] and Ingold's[13] interpretations as unacceptable. Moreover, Leffek denies the very idea of two ion pairs different in nature, whereas Gordon considers the special salt effect as a test of SSIP formation. Dannenberg[14] also objects to the existence of SSIP as a kinetically independent particle. He considers the special salt effect to be determined by the fact that ClO_4^- substitutes the solvent molecule, solvatizing the rear of the cationoid intermediate. As an argument in favour of the above he reports that during the acetolysis of cyclohexyltozylate with increasing perchlorate concentration the substitution/elimination ratio is growing (the result of intermediate stabilization) alongside with the growth of the relative yield of the substitution product with preserved configuration (hindrance of the rear-oriented attack)[15]. These data are in fair agreement with our interpretation of the special salt effect[2] based on the formation of $ClO_4^-|S|Ph_2CH^+Br^-$.

Kinetic parameters of Ph_2CHBr heterolysis in $PhNO_2$ and Me_2CO in comparison with similar information for t-BuBr[16,17] are presented in Table 3. Ph_2CHBr and t-BuBr heterolysis rates as well as those in other aprotic solvents[4] are similar. In the transition from $PhNO_2$ to Me_2CO the rate of Ph_2CHBr heterolysis slightly increases whereas that of t-BuBr falls. This seems to be a manifestation of Ph_2CHBr sensitivity to the electrophilic assistance[2] of acetone enol (the formation of $Ph_2CHBr \dashrightarrow HOC(Me) = CH_2$). In the transition from t-BuBr to Ph_2CHBr both the enthalpy and the entropy of activation decrease. Enthalpy decrease suggests the formation of a more stable carbocation in the case of Ph_2CHBr. Entropy decrease seems to be determined by the fact that t-BuBr heterolysis in aprotic solvents is limited by IIP formation[2] whereas Ph_2CHBr in the transition state requires additional coordination of the solvent molecule in $Ph_2CH^+Br^-$ interion space (SSIP formation)[3].

As opposed to aprotic solvents, the heterolysis of benz-

hydryl derivatives in polar protic solvents reaches the carbocation. This is suggested by the mass action salt effect[5,9,13,18]. Some papers indicate that S_N1-substitution in benzhydryl derivatives in polar aprotic solvents (DMF[19], Me_2CO[20], MeCN[21], $MeNO_2$[22] and others[23]) may proceed through the intermediate carbocation as well. As a rule, however, these suggestions are not substantiated. Only for the reaction of monomolecular nucleophilic substitution of bromine in Ph_2CHBr (the action of Et_4NCl and various amines) in $MeNO_2$ solution the arguments are given that are based on the rate depression in the presence of the salt with the common ion (Et_4NBr)[22]. However the effect of salts with a

Table 3

Kinetic Parameters of Ph_2CHBr and t-BuBr Heterolysis in Acetone and $PhNO_2$

Solvent	Substrate	$-\lg k_{25}(s^{-1})$	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}_{25}$ e.u.	$\Delta G^{\neq}_{25}$ kcal/mol
Me_2CO	Ph_2CHBr	6.82	15.8	36.9	26.8
	t-BuBr	7.13	19.5	28.5	27.2
$PhNO_2$	Ph_2CHBr	7.39	16.2	37.9	27.5
	t-BuBr	6.95	20.3	22.2	26.9

non-common ion has not been studied (the perchlorate is not considered , since it always increases the reaction rate). We have shown[2] that the heterolysis rate of Ph_2CHBr in MeCN being close in its polarity to $MeNO_2$ (ε38.6, Z 71.2) decreases both in the presence of salts with common and non-common ions (Cl^-, J^-, NO_3^-). The above is a manifestation of the negative salt effect rather than that of the acting mass law. Therefore the carbocation formation in $MeNO_2$ has not been confirmed. The rates of IIP formation from t-BuBr and those of SSIP formation from Ph_2CHBr were shown to be close[4]. The same was observed in $MeNO_2$ for t-BuBr[24], $\lg k_{25}(s^{-1}) = -5.4$, and Ph_2CHBr[22] $\lg k_{25} = -4.8$. If the heterolysis of Ph_2CHBr in $MeNO_2$ led to a free carbocation, the rate of this

reaction would be considerably lower than the rate of t-BuBr heterolysis. It means that both in $MeNO_2$ and other aprotic solvents SSIP formation is the rate limited step.

Three different salt effects, common, special and negative, are known to accompany IIP conversion into SSIP. At present it is already clear that all of them are specific. Indeed, they depend upon the nature of the cation[7,9,20,26-29], the anion[9,13,20,26-29], the solvent [18,26,27] and the substrate[27,28] being also influenced by the temperature[5]. Palm[30] stresses strong dependence of the salt effect on salt ionization degree. The common (usual) salt effect is often regarded as the salt effect of ion force[5,12]. It is not clear, however, how to distinguish this effect and the specific action of ions and/or ion pairs. As a rule, the negative salt effect is observed in aqueous-organic solvents[27-29,31,32]. Recently it has been found[18] during p,p'-dichlorbenzhydryl chloride solvolysis in the mixture of EtOH-CF_3CH_2OH. The above effect is insignificant ($\leq$30%) and is accounted for a decrease in the activity coefficient of the substrate. We have shown[2,3] this effect to be considerably higher in aprotic solvents.

As a rule, the intensity of the special and usual salt effect increases with a decrease in cation size[2,3,5,7,9,26]. Considering that ion pairs possess greater activity[33], the above fact could be accounted for the increase in the salt ion association degree. At present, however, the most widely accepted viewpoint is that the ions and ion pairs have equal activity[7,34]. This conclusion is in good agreement with the observation of the linear increase in the reaction rate with increasing analytical salt concentration.

An increase in salt activity with a decrease in cation size is most frequently explained by an increase in the intensity of electrophilic heterolysis assistance[7,25,35]. S_N1 and E1 reactions are known to be very sensitive to the electrophilic catalysis[5,35,36]. This effect, however, has never been confirmed for alkaline metal cations whereas for the ammonium ones it is impossible because the latter are unable to coordinate with anions. In work [37] the alkaline met-

al ions were shown not to activate t-BuBr hydrolysis (rate-determining SSIP formation[4]). During the anion exchange in p-Cl-benzhydrylchloride in acetone[20] and t-BuCl solvolysis in 70% MeOH[38] (rate-determining SSIP formation[4]) the intensity of the salt effect increased in the transition from $Li^+(Na^+)$ to $Bu_4N^+(NH_4^+)$. Thus, the suggestion of electrophilic assistance is of little use for the cation salt effect interpretation.

The increase in the intensity of the special and usual salt effects with a decrease in cation size and the fall of the former in case of the negative salt effect has been interpreted by us[2] through the formation of non-active cationoid triplets ($Ph_2CH^+Br^-/S/M^+$), the stability of which increases with an increase in cation size. The above conclusion has been based on the following fact. During the Ph_2CHBr heterolysis in MeCN the intensity of the negative salt effect increases as follows:

LiBr (1.5) < Et_4NBr (1.9) < Et_4NJ (2.1) < Bu_4NJ (2.6) ≈ Vd^+Br^- (2.6) < N-butylquinolinium-iodide (3.4) - the figures in brackets indicate the factor by which the rate constant decreases at 2.10^{-4}M salt concentration at 25°C*). It may be seen that the bigger the cation, the greater is the effect. There are two possible explanations for this dependence: either electrophilic heterolysis assistance, having the maximum level for Li^+, or the non-active triplet formation, the stability of which grows with an increase in cation size. The comparison of the values in the given series of salts shows that at $[Li^+] = 2.10^{-4}$M the Ph_2CHBr heterolysis rate should increase not less than 2-fold due to Li^+ catalytic action. In work[2] the reaction rate at $[LiClO_4] = 2.10^{-4}$M was shown to remain practically unchanged, i.e. the electrophilic assistance of Li^+ was shown to be missing. Thus, the specific cation effect in our case is determined by the formation of non-active triplets with the substrate IIP.

To confirm this conclusion we have made a number of experimental runs in the presence of dibenzo-18-crown-6. The

*) Under these conditions the salts dissociate completely[2].

conditions and results of these kinetic runs are presented in Table 4. It may be seen, crown additions (run 2) have no effect on the reaction rate, determined against Vd$^{\cdot}$ consumption. The rate in this case satisfactorily coincides with the previous determination[2] (the last column of the Table 4, run 1). The crown additions in the presence of $LiClO_4$ (runs 3 and 4) and LiBr (runs 5 and 6) practically exert no effect on the reaction rate. The stability constant of Li^+ complex with dibenzo-18-crown-6 in propylene carbonate at 25°C is $\sim 2 \cdot 10^3$ l/mole[39]. If we adopt the same value for MeCN *), then in our runs Li^+ should be by 50–85 % bound in a complex. This is sufficient for the manifestation of the effect.

Table 4

Kinetics of Ph_2CHBr Ionization in MeCN in the Presence of Salts and Dibenzo-18-crown-6

Nos.	[Vd$^{\cdot}$]·$\cdot 10^4$M	[Ph_2CHBr]·$\cdot 10^3$M	[crown]·$\cdot 10^3$M	Salt addition		$10^6 \cdot k, s^{-1}$	$10^6 \cdot k^{a)}, s^{-1}$
				nature	[MX]·$\cdot 10^3$M		
1	0.980	6.90	-	-	-	2.68±0.21	2.50
2	1.34	5.74	15.8	-	-	2.77±0.05	-
3	1.26	6.65	4.90	$LiClO_4$	4.07	3.20±0.18	3.25
4	1.36	4.90	21.0	$LiClO_4$	20.3	4.73±0.15	4.60
5	1.14	7.41	0.832	LiBr	0.816	0.930±0.021	0.900
6	1.41	7.24	1.67	LiBr	1.63	0.722±0.04	0.700

a) Values of constants without addition of the crown capture from the papers [1,2].

Thus, the following conclusions can be drawn: a) the special salt effect is determined by ClO_4^- action; b) the negative salt effect is mainly determined by the action of

*) In MeCN this value should be somewhat higher[39] since this solvent is less polar and has a lower donor number (DN 14.1), than propylene carbonate (ε 70.0, Z 72.5, DN 15.1)[40].

salt anions and c) the amount of cation effect (weakening of the special salt effect and strengthening of the negative salt effect) increases with the growing cation size.

The results of this and our previous papers[1-4,41] as well as the information on salt effects for benzhydryl systems available in literature may be generalized using scheme (4), which reflects the effect of salts on the IIP conversion into SSIP. The main reason for the usual salt effect seems to be the quadrupole formation between the IIP of the substrate and SSIP of the salt (Q_s)*). In this quadrupole the salt facilitates further charge separation in the substrate and leads to the formation of the quadrupole consisting of two SSIP (Q_{ss}). Such a quadrupole may disintegrate forming SSIPs III and III_y, which then rapidly form the products. Q_s quadrupole formation may proceed along three different paths. It forms either in the interaction of IIP substrate with the ion pair of the salt or via the successive association with the salt ions**) with the intermediate formation of cationoid (IV_s^+) and anionoid ($_sIV^-$) triplets***). The above explains, why a linear increase of the usual salt effect with an increase in analytical salt concentration is observed.

The special salt effect is determined by nucleophilic or electrophilic contribution of the salt into the substrate heterolysis. The cation special salt effect has been observed[9] with the action of $Co(NO_3)_2$. The effect is small, $k_s^o/k = 1.3$. Co (II) is a relatively strong complex forming agent [35,44]. The stability constant of Li^+ complexes is lower by many orders of magnitude as compared with that of Co.[45] The above explains the unability of Li^+ to contribute electrophilically to the heterolysis of benzhydryl derivatives. Electro-

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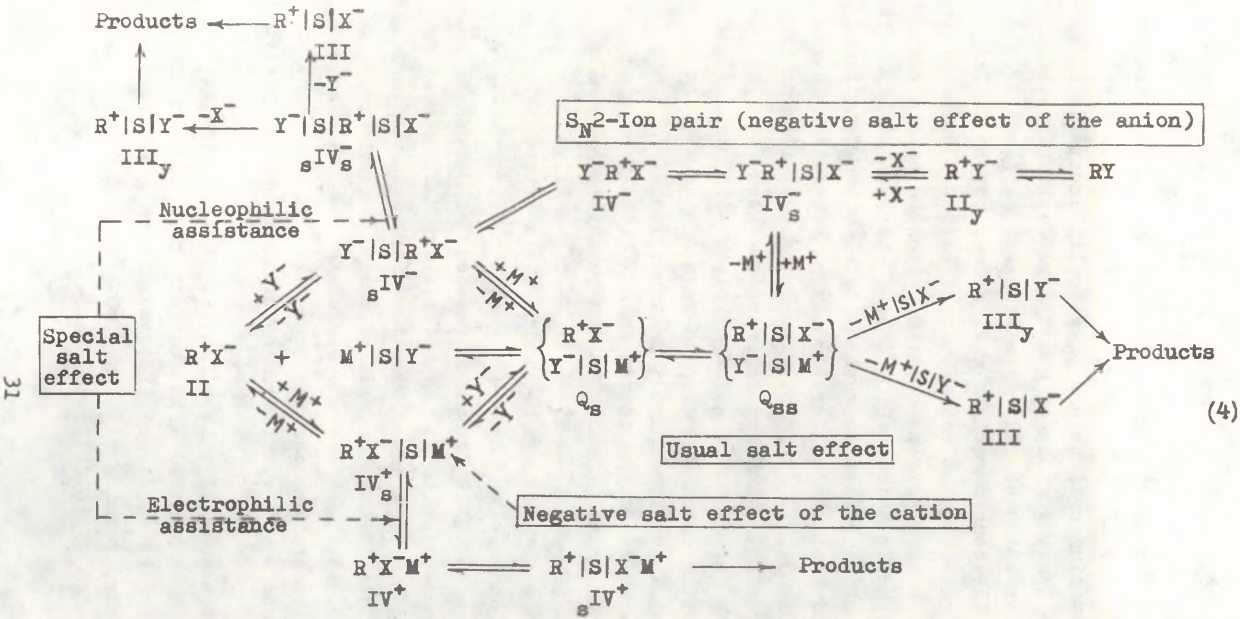
*) At high salt concentrations the catalysis with more complex aggregates is possible[42].

**) Push-pull mechanizm of the catalysis ($Y^-|S|R^+X^-|S|M^+$ formation) is not excluded.

***) Initial formation of a solvent-separated ion bond at the salt ion side is always presupposed.



(4)

General scheme of salt effects at the transition from the intimate ion pairs to the solvent-separated one

philic catalysis of the cation should be performed via an intermediate intra-sphere complex[33] (IV^+). Metal ion coordination with the leaving group facilitates further charge separation in the IIP substrate ($_sIV^+$ formation). Alkaline metal and ammonium cations are practically incapable to coordinate the leaving group of benzhydryl derivatives, that is why the formation of $_sIV^+$-type triplets may lead to a decrease in IIP concentration[5] and, hence, to the falling heterolysis rate (cation negative salt effect). Nucleophilic catalysis of heterolysis is observed with the action of large easily polarizable anions (ClO_4^-, N_3^-, ^-OTs)[1-4,8,12,41]. The association of such ions increases the electron density of R^+X^- bond and facilitates further charge separation in IIP ($_sIV_s^-$ formation). $_sIV_s^-$ triplet then decomposes forming ion pairs III or III_y, which are rapidly converted into the products. The formation of anion triplets with small rigid anions may bring about the displacement of the solvent molecule from the inter-ion space (the formation of IV^-) and further separation of the charge in R^+X^- (the formation of IV_s^-) - the nucleophilic substitution reaction, S_N2 - ion pair, occurs ($II \rightarrow {}_sIV^- \rightarrow IV^- \rightarrow IV_s^- \rightarrow II_y \rightarrow RY$). The same substitution mechanism may be realized also through the intermediate quadrupole ($II \rightarrow Q_s \rightarrow Q_{ss} \rightarrow IV_s^- \rightarrow$ etc.). In both cases the SSIP formation rate will fall due to partial IIP consumption in S_N2 reaction, which is observed as the reaction rate decreases, monitored through the verdazyl. Under these conditions the rate of substrate conversion is very low (~0.1%), therefore the appearance of the covalent substrate with another leaving group (RY) in the reaction medium can not exert considerable influence on the reaction rate.

Lack of the special salt effect of the perchlorate in acetone may be connected with the fact that further charge separation in the substrate IIP occurs with greater ease in the quadrupole, forming with the C=O group of the solvent, than in the $ClO_4^-/S/Ph_2CH^+Br$-triplet.

EXPERIMENTAL

The reagents were obtained and purified as earlier[1]. Dibenzo-18-crown-6 was purified by multiple recrystallization from benzene and i-PrOH, m.p. 164° (see Ref.[39]). Acetone was dried over $CaCl_2$, kept over P_2O_5 for 2 hrs with fresh anhydride additions after each 20 min., decanted, kept over potash and rectified (for Vd$^+$ in acetone λ_{max} 710 nm, ε 4009). Nitrobenzene was purified by double distillation (for Vd$^+$ $\lambda_{max.}$ 720 nm, ε 4570). The salts were kept in a desiccator over P_2O_5. Kinetic runs were performed as in Ref.[1-4]. The reaction rate was monitored spectrophotometrically against Vd$^+$ consumption. Individual runs confirmed that rate monitoring against Vd$^+Br^-$ formation gave similar results.

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INVESTIGATION OF THE STRUCTURE EFFECT ON THE KINETICS OF THE FORMATION OF TRIARYLMETHANE LEUCONITRILES IN WATER

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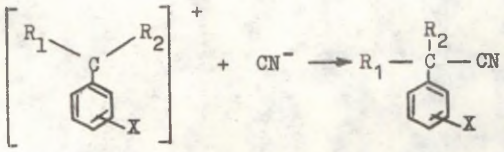
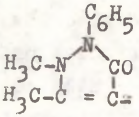
The spectrophotometric study of the kinetics of the formation of leuconitriles of derivatives of Malachite Green and its diantipyrine analogues in water in the temperature range II.5-40°C has been carried out. Isokinetic relationship is shown to exist in the reaction series studied, with the prevailing of enthalpy (β =345K) and entropy (β =222K) factor, respectively. The results obtained are given in comparison with the data for the reaction of triarylcarbinol formation.

Continuing the investigation of the structure effect on the reactivity of the conjugated carbonium ions [1-3], we have studied the kinetics of the formation of leuconitriles of a number of Malachite Green (I) and Antipyrine Orange (II) derivatives in water in the temperature range II.5-40°:



I: $R_1=R_2=$ 4-$(CH_3)_2NC_6H_4$ X: 4-CH_3; 3-CH_3; H; 3-Cl; 3-NO_2; 4-NO_2;

II: $R_I = R_2 =$ 

X: 4-CH_3; 3-CH_3; H; 4-Cl; 3-Br; 3-NO_2.

Both the bimolecular rate constants and the activation parameters are listed in Tables 1 and 2.

Table 1

KINETIC PARAMETERS OF THE PROCESS OF FORMATION OF LEUCONITRILES OF MALACHITE GREEN DERIVATIVES

R	Rate constants, l/mol·s					$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J/mol·K
	15°C	20°C	25°C	30°C	40°C		
4-CH_3	0.233	0.365	0.542	0.743	1.46	52	75
3-CH_3	0.262	0.400	0.577	0.808	1.54	50	80
H	0.280	0.447	0.652	0.936	1.63	49	83
3-Cl	0.405	0.590	0.828	1.09	1.87	43	101
3-NO_2	0.542	0.791	1.07	1.32	2.30	40	110

Table 2

KINETIC PARAMATERS OF THE PROCESS OF FORMATION OF LEUCONITRILES OF ANTIPYRINE ORANGE DERIVATIVES

R	Rate constants, l/mol·s					$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J/mol·K
	11.5°C	15°C	20°C	30°C	40°C		
4-CH_3	10.6	12.7	17.8	28.5	45.7	35	100
3-CH_3	14.0	16.0	22.1	37.6	63.1	37	91
H	15.1	17.5	24.7	42.9	75.3	39	86
4-Cl	23.2	29.0	39.4	73.3	126	42	71
3-Br	29.2	37.9	53.5	103	166	43	64
3-NO_2	50.2	63.4	94.4	180	363	49	40

Relative errors of the rate constants do not exceed ± 2% uncertainties of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are within ± 2kJ/mol, ± 4 J/mol·K, respectively.

The Hammett equation is found to describe the substituent effect on the rate constant of the process under consideration over the whole temperature range studied, the reaction constants being close to the corresponding values for the reaction of the triarylcarbinol formation (Table 3) [1-3].

Table 3

CORRELATION PARAMETERS FOR THE REACTION OF FORMATON OF LEUCONITRILES OF MALACHITE GREEN (I) AND ANTIPYRINE ORANGE (II)

Series	Temperature	ρ	lg k_o	r	s
I	15°C	0.426 ± 0.009	-0.555 ± 0.004	0.999	0.009
	20°C	0.363 ± 0.011	-0.366 ± 0.005	0.998	0.010
	25°C	0.333 ± 0.012	-0.205 ± 0.006	0.997	0.011
	30°C	0.295 ± 0.009	-0.076 ± 0.004	0.998	0.008
	40°C	0.220 ± 0.009	0.204 ± 0.004	0.996	0.008
II	11.5°C	0.746 ± 0.024	1.178 ± 0.009	0.998	0.018
	15°C	0.796 ± 0.026	1.255 ± 0.009	0.998	0.020
	20°C	0.824 ± 0.012	1.398 ± 0.004	0.999	0.009
	30°C	0.912 ± 0.034	1.634 ± 0.012	0.997	0.025
	40°C	0.989 ± 0.015	1.852 ± 0.003	0.997	0.021

As should be expected, in both series studied exists the isokinetic relationship, such a conclusion being confirmed by the following criteria:

I. The temperature dependence of the reaction constants [4,5]:

$$\rho = (-2.11 \pm 0.11) + (729 \pm 33)\,\frac{1}{T} \qquad \text{(series I)}$$

$n = 6$; $r = 0.997$; $s = 0.07$;

$\rho = (3{,}36 \pm 0.009) - (741 \pm 28)\cdot\frac{I}{T}$ (series II)

$n = 6$; $r = 0.998$; $s = 0.07$.

gives the values of β 345K (series I) and 222K (series II)

2. The extrapolated Arrhenius equations are crossed at 345 ± 5 K (I) and 222 ± 5 K (II).

3. The linearity between the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values [4,5] with the slope 345K and 222K, respectively:

I: $\Delta H^{\neq} = (78.2 \pm 0.2)\ 10^3 + (345 \pm 3)\cdot\Delta S^{\neq}$

$n = 6$; $r = 0.999$; $s = 0.023$;

II: $\Delta H^{\neq} = (57.7 \pm 0.2)\ 10^3 + (222 \pm 2.5)\cdot\Delta S^{\neq}$

$n = 6$; $r = 0.999$; $s = 0.029$.

4. The linearity between $\Delta H^{\neq}$ and $\lg k_T$ [6]:

I: $\Delta H^{\neq} = (35.6 \pm 0.6) - (37.9 \pm 1.9)\ \lg k_{20^\circ C}$

$n = 6$; $r = 0.995$; $s = 0.15$; $\beta = 344K$

II: $\Delta H^{\neq} = (13.6 \pm 1.4) + (17.6 \pm 0.9)\ \lg k_{20^\circ C}$

$n = 6$; $r = 0.995$; $s = 0.13$; $\beta = 222K$

5. The Exner criterion (linearity of lgk values determined at two different temperatures)[7]:

I: $\lg k_{30^\circ C} = (0.307 \pm 0.003) + (0.691 \pm 0.07)\ \lg k_{15^\circ C}$

$n = 6$; $r = 0.999$; $s = 0.003$; $\beta = 343K$

II: $\lg k_{40^\circ C} = (0.294 \pm 0.035) + (1.326 \pm 0.027)\ \lg k_{11.5^\circ C}$

$n = 6$; $r = 0.999$; $s = 0.015$; $\beta = 222K$

6. The two-parameter equation $\lg k = f(\delta, T)$:

I: $\lg k = (8.89 \pm 0.03) - (2717 \pm 89)\frac{I}{T} - (2.11 \pm 0.11)\delta + (728.8 \pm 32.9)\delta\cdot\frac{I}{T}$

II: $\lg k = (8.66 \pm 0.13) - (2131 \pm 38)\frac{I}{T} + (3.36 \pm 0.09)\cdot\delta - (741.0 \pm 28.2)\delta\ \frac{I}{T}$

The values of isokinetic temperatures, counted from these equations, are 345K and 220.5K, respectively.

The latter equations predict two more isoparametric points at which the rate constant should not depend on temperature [8]:

I:	$\hat{\sigma}_I = 3.73$	$\hat{\sigma}_2 = 4.21$
II:	$\hat{\sigma}_I = -2.88$	$\hat{\sigma}_2 = -2.58$

Thus all the criteria cited above lead to the conclusion that the isokinetic relationship works in both series under consideration with the β values 345K and 222K, respectively.

It should be mentioned that similarly to the reaction of the formation of triarylcarbinols, series I is characterized by the prevailing of activation enthalpy ($\beta > T_{exp}$) and series II by the prevailing of activation entropy ($\beta < T_{exp}$). Such a result completely agrees with the understanding of connection between the internal (electron) and external (solvatation) factors in stabilization of carbocations [9], according to which the shortening of the conjugated system of carbocations at transition from Malachite Green derivatives to their diantipyrine analogues must be accompanied by an increase of the δ^+ -charge on the carbon center and corresponding increase of the solvation stabilization.

Thus the type of the control of the reactivity of the conjugated ions is mainly determined by the δ^+-charge of the carbonium center and does not depend on the nucleophile nature.

EXPERIMENTAL

The kinetic investigation has been carried out spectrophotometrically by means of a SF-26 -spectrophotometer, supplied with a thermostated block. The temperature deviations were in the range of 0.1°. Registration of the kinetic curves was made on the wavelength of the maximum absorbance of the dyes by automatic recorder.

Alkali was added to stock solutions to diminish the hydrolysis of the cyanide ion. When calculating the rate constants of the process studied the corresponding values for reaction with the hydroxide ion[3] were substracted from the experimental values. After that the rate constants obtained for the primary salt effect were corrected.

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CATALYTIC ACTIVITY OF N-ACYLAMINOACID ESTERS IN THE REACTION OF PEPTIDE BOND FORMATION

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Catalytic activity of N-benzoyl and N-phtalyl-aminoacid esters as well as a number of representatives of tertiary amines and amides have been studied in the reaction of peptide bond formation by the method of activated esters in benzene. It was shown that in histidine and glutamic acid derivatives which have higher activity, the imidazole fragment and the carboxyl group are responsible for the catalysis. The catalytic activity of other derivatives is remarkably lower and it is conditioned by the participation the amide group in the process which occurs according to the mechanism of the general base catalysis.

To understand the functioning mechanism of enzymes it is useful to study relatively simple model systems which express some more characteristic properties of the reactions catalyzed by enzymes. Recent research has shown that active enzyme centers contain hydrophobic areas. This accounts for the fact that the enzymic reaction proper proceeds in the medium of low dielectric permittivity[1-3]. Therefore research into model reactions in aprotic media of low polarity is of special interest, the reactions of acyl transfer in particular. Such research is necessary to elucidate the peculiarities of reaction mechanisms which proceed in nonaqueous aprotic media,

by comparison with the corresponding processes in water for which considerable experimental data have been obtained and generalizations have been made (see, e.g., references 4-6).

The present work aims at observing the catalytic behavior of functional groups which are included in active enzyme centers (the amide group of the polypeptide chain, the imidazole fragment, carboxyl and methilol groups, etc.) in the reaction of peptide bond formation. With this aim in view we have studied the catalytic activity of N-benzoylamino acid $C_6H_5CO-NH-CHR-COOR'$ esters with broad variation of the structure of the lateral group of the amino acid component $R(R'=CH_3)$ and the structure of the ester component $R'(R=H)$ of phthalylglycine ethyl and phenyl esters as well as a number of representatives of tertiary amines and amides in the reaction of carbobenzoxiglycine p-nitrophenyl ester (Z-gly-ONP) with glycine tert-butyl ester (tert-BEG) in benzene at 25°C:

$$C_6H_5CH_2OCO-NHCH_2COOC_6H_4NO_2 + NH_2CH_2COOC(CH_3)_3 \longrightarrow$$

$$\longrightarrow C_6H_5CH_2OCO-NHCH_2CO-NHCH_2COOC(CH_3)_3 + HOC_6H_4NO_2 \quad (1)$$

E X P E R I M E N T A L

Pure Z-gly-ONP[7], tert-BEG[7], benzene [8], ethylacetate[9], triethylamine[10], pyridine[11], dimethylformamide[12], dimethylacetamide[12], N-methylformamide[12], caprolactam[12] were prepared or purified by well-known methods. N-acylaminoacid esters were synthesized by two methods[13]: (A) by acylation of previously obtained hydrochlorides of amino acid esters; (B) by esterification of previously synthesized N-acylamino acids. Experimental conditions of ester synthesis are given in Table 1. The obtained compounds were recrystallized repeatedly (until constancy of melting points was achieved) from the corresponding solvents which have been indicated alongside with melting points of compounds in Table 1.

The process was monitored spectrophotometrically by the formation p-phthalylglycine in the solution at 320 mm on a SF-26, only in the case of N-phthalylglycine esters and methyl esters of

Table 1

Conditions of Synthesis and Temperature of Melting Points of N-acylamino Acid Esters (all the amino acids are racemic)

No	Compound	Method of Synthesis	Solvent for recrystallization	Melting point, °C	Reference melting point °C
1	2	3	4	5	6
1.	Bz-gly-OCH_3	A	CCl_4	81	79-81[14]
2.	Bz-ala-OCH_3	A	decane	82	
3.	Bz-val-OCH_3	A	cyclohexane	86-87	
4.	Bz-lei-OCH_3	B	cyclohexane	97-98	
5.	Bz-norleu-OCH_3	A	hexane	72-73	
6.	Bz-phe-OCH_3	A	cyclohexane	102	
7.	Bz-met-OCH_3	A	CCl_4	84	
8.	Bz-asp-OCH_3 / OCH_3	B	hexane	85	
9.	Bz-gly-OCH_3 / OCH_3	A	cyclohexane	83-84.5	
10.	Bz-glu-OH / OCH_3	A	CCl_4	82	
11.	Bz-pro-OCH_3	A	benzene	88-89	
12.	Bz-his-OCH_3	A	benzene	107	
13.	Bz-ser-OCH_3	B	hexane	163-164 (various)	
14.	Bz-gly-OCH_2H_5	A	CCl_4, hexane	62-62.5	60.5[15]
15.	Bz-gly-$OC(CH_3)_3$	A	CCl_4, hexane	114-114.5	109[16]
16.	Bz-gly-$OCH(CH_3)_2$	B	methanol hydrate	86-88	
17.	Bz-gly-$OCH_2C_6H_5$	B	CCl_4, hexane	89.5-90	88[16]

Table 1 (continued)

1	2	3	4	5	6
18.	Bz-gly-OCH(C_6H_5)$_2$	A	CCl_4	125-126	123-124[16]
19.	Bz-gly-OC_6H_5	B[17]	ethanol, hexane	106-106.5	104[17]
20.	Phth-gly-OC_2H_5	B	hexane	114-115.5	III[18]
					108-110[19]
					112[20]
21.	Phth-gly-OC_6H_5	B[17]	ethanol	121-122	120-121[21]
22.	Bz-gly-OCH$_3$ (OH)	B	ethylacetate	112-113	

N-benzoylhistidine measurements were carried out at 345 nm due to their remarkable absorption in this region. The reaction rate was studied in the conditions of pseudo-first order kinetics, the concentration of Z-gly-ONP ($a \approx 5 \cdot 10^{-5}$ mol/l) being much lower than that of tert-BEG (b=0.04 mol/l), i.e. at $a \ll b$. The variation range of catalyzer concentration (m, mol/l) is displayed in Table 2. The observed second order rate constants (k_{obsd}, l/mol-sec) were calculated in accordance with the formula:

$$k_H = \frac{2.3}{bt} \lg \frac{D_\infty - D_o}{D_\infty - D_t}, \qquad (2)$$

where D_o, D_t and D_∞ stand for optical density of the solution at the initial stage (D_o), at a certain moment t and (D_t) and later when the reaction has practically ended (D_∞). Methods of mathematical statistics were applied to treat linear relationships.

Table 2

Rate constants k_m ($l^2/mol^2 \cdot sec$) of the reaction of Z-gly-ONP with tert-BEG, catalyzed by N-benzoylamino acid methyl esters $C_6H_5CO-NH-CHR-COOCH_3$(Nos.1-9,11,12) by hippuric acid $C_6H_5CO-NHCH_2COOR'$ esters(Nos.13-18) and by a number of ether organic bases; benzene, at 25°C*.

No	Catalyzer	$k_m \cdot 10^3$, $l^2/mol^2 \cdot sec$	Range of concentration change of the catalyzer m, mol/l
1	2	3	4
1.	Bz-gly-OCH_3 R= H	59.9±0.1	0.005-0.08
2.	Bz-ala-OCH_3 R= CH_3	26.6±0.1	-"-
3.	Bz-val-OCH_3 R= $CH(CH_3)_2$	21.0±1.0	-"-
4.	Bz-lei-OCH_3 R= $CH_2CH(CH_3)_2$	12.6±2.5	-"-
5.	Bz-norleu-OCH_3 R= H-C_4C_9	25.2±0.9	-"-
6.	Bz-phe-OCH_3 R= $CH_2C_6H_5$	52.6±0.1	-"-
7.	Bz-met-OCH_3 R= $CH_2CH_2SCH_3$	158±3	-"-
8.	Bz-asp-OCH_3 / OCH_3 R= CH_2COOCH_3	273±80	-"-
9.	Bz-glu-OCH_3 / OCH_3 R= $CH_2CH_2COOCH_3$	65±3	-"-
10.	Bz-glu-OH** / OCH_3 R= $CH_2CH_2COOCH_3$	1080±90	-"-
11.	Bz-pro-OCH_3	36.0±1.4	-"-
12.	Bz-his-OCH_3 R= CH_2-(imidazole)	251±36	-"-
13.	Bz-gly-OC_2H_5	31.5±1.2	0.04-0.12
14.	Bz-gly-$OCH(CH_3)_2$	9.6±1.6	0.01-0.08
15.	Bz-gly-$OC(CH_3)_3$	35.6±3.9	0.02-0.08
16.	Bz-gly-OC_6H_5	212±27	0.005-0.02
17.	Bz-gly-$OCH_2C_6H_5$	80.8±7.6	0.03-0.12
18.	Bz-gly-$OCH(C_6H_5)_2$	530±18	0.0025-0.01
19.	Phth-gly-OC_2H_5	239±10	0.02-0.12

Table 2 (continued)

1	2	3	4
20.	Phth-gly-OC_6H_5	57.2 ± 2.6	0.02-0.12
21.	Dimethylformamide	57.6 ± 2.6	0.01-0.08
22.	Dimethylacetamide	68.1 ± 3.1	0.01-0.06
23.	N-methylformamide	39.1 ± 2.4	0.01-0.08
24.	Caprolactam	427 ± 23	-"-
25.	Z-gly-gly-OBu-t***	114[2]	-
26.	Ethylacetate	0	0.01-0.06
27.	Triethylamine	44.4 ± 2.4	0.01-0.08
28.	Pyridine	30.8 ± 1.0	-"-
29.	Imidazole	490[22]	-
30.	N-methylimidazole	490[22]	-
31.	tert-BEG	129[7]	-
32.	Pyrazole	1740[23]	-
33.	Acetic acid	710000[24]	-
34.	2-Oxipyridine	5600[25]	-

*) Due to the insolubility of B_z-ser-OCH_3 (No 13 in Table 1) and Bz-glu-OCH_3 (No 22 in Table 1) it was not possible to study their catalytic activity in benzene.

**) With catalyzer No 10 the experiment and data treatment were carried out according to the method described in references 24 and 26.

***) tert-Butyl ester of carbobenzoxiglycylycine.

DISCUSSION AND RESULTS

It has been shown earlier[24] that in the conditions of a pseudo-first order reaction the observed bimolecular rate constants (k_H^o) of the reaction of Z-gly-DNP with tert-BEG in benzene in the absence of the added catalyzer can be described by the following equation:

$$k_H^o = k_o + k_b \cdot b \quad , \qquad (3)$$

where k_o (l/mol·sec) and k_b ($l^2/mol^2 \cdot sec$) are the rate constants for the noncatalytic and catalyzed second molecule

tert-BEG reactions respectively.

In the presence of organic catalysts with the exception of imidazole[22] and N-benzoylglutamic acid γ methyl ester (No 10, Table 2) (cf. references 24 and 26), the equation for the observed rate constant k_H is as follows:

$$k_H = (k_o + k_b.b) + k_m.m = k_H^o + k_m.m \ , \qquad (4)$$

where k_m ($l^2/mol^2.sec$) is the rate constant of the trimolecular reaction, conditioned by the catalyzer. From this equation it is easy to calculate the k_m value on the basis of linear dependence of k_H on m under experimental conditions at the constant concentration of amine b.

k_m values for all the studied catalyzers are displayed in Table 2.

The majority of catalyzers in Table 2 are amides (Nos. 1-25); N-acylaminoacid esters, which model the peptide fragment and contain also an ester grouping.Therefore in the first place it was made clear which grouping in these compounds - amide or ester - was responsible for catalysis.It appeared that the activity of the above compounds is close to the activity of carboxylic acid amides (cf.Nos.1-9,11-20 with Nos. 21-24), which do not contain the CO group of esters, at the same time ethylacetate (No.26) exerts no influence whatsoever on the peptide formation rate. Thus, it is the amide group that is responsible for catalysis.

It should also be noted that the catalytic activity of amide group containing compounds which are characterized by extremely low basicity ($pK_a \lesssim 0$) is close to those which are rather basic compounds like tertiary amines (triethylamine, pK_a 10.87; N-methylimidazole, pK_a 7.33; imidazole, pK_a 6.95; pyridine, pK_a 5.23). Besides, for a number of bases for which we have found data on K_{BH} values in the literature, a symbatic relationship (see Fig.1) occurs between lgk_m and pK_{BA}, where K_{BH} is the constant for hydrogen bond formation between the base-catalyzer and a standard proton donor (in

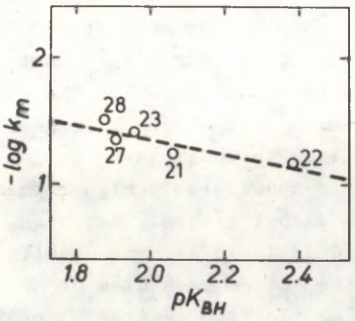


Fig.1. The dependence of log k_m on pK_{BH} for the reaction of Z-gly-ONP with tert-BEG catalyzed by bases, benzene, 25°C. The numbering corresponds to that of Table 2.

the present case fluorophenol) under standard conditions (CCl_4, 25°C) [27,28]. It is typical that the data for amides* as well as for nitrogen bases are satisfactorily linear. It has been assumed[29], that the presence of the type represented in Fig. 1 indicates the general basicity mechanism of the catalysis. It means that the base-catalyzer contributes to the proton transfer from the acylyzed NH_2 group to the leaving group during the rate determining step.

It is of interest that imidazole, which models a fraction of the active center of many proteolytic enzymes is as active as N-methylimidazole (ch. No 29 with No 30), but at the same time it does not differ notably for its activity from other tertiary amines (see Nos. 27 and 28). It is noteworthy that the catalytic rate constant for benzoylhistidine methyl ester (No 12) is nearly the same as for imidazole (No 29). Consequently, the catalytic effect for compound 12 unlike other benzoylamino acid esters (Nos. 1-10) is caused by the imidazole and not by the amide fragment.

It should be noted that general basic catalysers due to their action in the studied reaction of peptide formation are remarkably inferior to the catalyzers of bifunctional

* Unfortunately no data on the associations of compounds 1-20 with any proton donors can be found in the literature, It is for this reason why Fig.1 displays only the results on carboxylic acid amides.

nature, such as carboxylic acids, 2-oxipyridine, pyrazole (see Nos. 32-34). The effect of the active acid is particularly high (No 33) which has been scrutinized in a number of our earlier papers[24,26]. It becomes clear that the catalytic activity of benzoylglutamine acid γ methyl esters (No 10), which contain in addition to the amide grouping also a free carboxylic group, is considerably higher than that of other benzoylaminoacid methyl esters. The high activity of bifunctional compounds is in accordance with the current understanding of the action mechanism of the active centers of a number of proteolytic enzymes according to which two or more fragments of the protein molecule simultaneously participate in the catalytic act. The latter provide the concerted change in the reacting bonds in the cyclic transitional state[30,31].

Since the activity of N-benzoylamino acid C_6H_5CO - - $NHCHRCOOCH_3$ methyl esters has been studied for a great number of amino acids, it is of interest to observe how it depends on the lateral part of amino acid R. The comparison of log k_m with σ^* parameters which characterize the induction effect of substituent R as well as with E_s^o parameters which characterize their steric influence* shows that both of the above mentioned effects influence the catalytic activity of the considered derivatives. Therefore the data for a number of N-benzoylaminoacid methyl esters (Nos. 1-6,8,9) were treated according to the two-parameter equations:

$$\lg k_m/k_m^o = \rho^* \sigma^* + \delta E_s^o , \qquad (5)$$

where σ^* and E_s^o are the empirical induction and steric constants for substituent R; ρ^* and δ are the sensitivity of the catalytic reaction rate due to the induction and steric effects of

* σ^* and E_s^o values for R (Nos.1-6) have been taken from ref.32; σ^* for Nos.8,9 from ref.33; E_s^o for Nos.8,9 have been taken as equal to E_s^o of substituents $CH_2CH(CH_3)_2$ (-1.13) and $CH_2CH_2CH(CH_3)_2$ (-0.55)[34] which are isosteric to them.

substituent R in the molecule of the catalyzer; k_m^o is the rate constant for the reaction which is catalyzed by the "standard" catalyst ($R=CH_3$). We have obtained the following correlation parameters in accordance with equation(5):

$$\lg k_m = (-1.64\pm0.09) + (1.12\pm0.16)\sigma^* - (0.11\pm0.11)E_s^o \quad (6)$$

$$R = 0.953; \qquad S_{obsd} = 0.147; \qquad n = 8.$$

With the exception of point No 4 the correlation parameters improve:

$$\lg k_m = (-1.63\pm0.04) + (1.00\pm0.007)\sigma^* - (0.22\pm0.05)E_s^o \quad (7)$$

$$R = 0.991; \qquad S_{obsd} = 0.0614; \qquad n = 7.$$

The influence of R' substituents in the substituted esters of the hippuric acid $C_6H_5CO\text{-}NHCH_2COOR'$ (Nos.1, 13-18) on their catalytic activity can also be expressed by equation (5) with the following correlation parameters:

$$\lg k_m = (-1.51\pm0.01) + (1.60\pm0.32)\sigma^* - (0.21\pm0.10)E_s^o \quad (8)$$

$$R = 0.929; \qquad S_{obsd} = 0.259; \qquad n = 7.$$

With the exception of point No 14 the correlation parameters improve notably:

$$\lg k_m = (-1.40\pm0.09) + (1.36\pm0.20)\sigma^* - (0.20\pm0.06)E_s^o \quad (9)$$

$$R = 0.972; \qquad S_{obsd} = 0.144; \qquad n = 6.$$

It can be concluded from the absolute values of ρ^* and δ that the catalytic activity of the considered catalyzer depends very little on the steric properties of substituents R and R' and is determined first and foremost by their induction effects.

It is of great interest to consider the sign of ρ^* and δ values. It should be noted that δ hardly deserves any interest due to its low absolute value. Nevertheless, its negative sign gives evidence of a certain steric contribution to the catalysis from the part of R and R' in N-acylamino

acid esters. This fact is rather surprising from the point of view of general basic catalysis of the amide grouping.

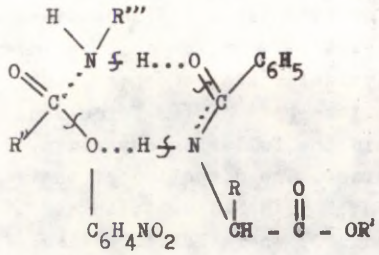
However, it is even more surprising that on the one hand the catalytic activity of the considered series of catalyzers is rather sensitive to the influence of the induction effect of R and R' substituents and on the other hand the sign of ρ^{*} is positive. The latter indicates that catalytic effectiveness improves with an increase in electron acceptor properties of R and R' substituents. Considering the general basic mechanism of the C=O amide group catalysis this fact is also unexpected.

As the N-acylamine acid esters studied in the present work are N-monosubstituted amides, i.e. they contain a N-H bond, we would like to relate the observed system of R and R' influence on their catalytic activity to the participation of the N-H grouping in the catalytic act, which fulfils the function of electrophilic solvation. However, this participation could be represented as the bifunctional catalysis of the amide grouping, similarly to the action of such compounds as carboxylic acids, 2-oxipyridine, etc.[24-26]

However, this assumption is unreliable for the following considerations. Firstly, the activity of N-acylamino acid esters is considerably lower than the activity of typical bifunctional catalyzers. Secondly, proceeding from the general regularities in the influence of substituents in amides on their conformation[35], it should be concluded that most probably for the studied catalyzers the trans position of C=O carbonyl and N-H groups in relation to the C-N bond should be more preferable. At such conformation of amides the bifunctional catalysis is in principle excluded due to the agreed participation of the above groups which require cis position in relation to the C-N bond to form the cyclic transitional state (see 1).

In our view the following hypothesis is more justified. It enables us to explain the observed sign of ρ^{*} in the framework of the general base catalytic mechanism of the C=O amide group catalysis of the peptide bond formation

process. On the basis of



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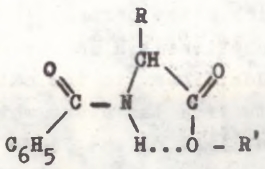

II

a number of observations[36-38] it could be concluded that the formation of the intramolecular hydrogen bond (IHB) is possible in N-monosubstituted amino acid esters, as is shown by structure II.

The presence of such a bond may further stabilize the trans position of C=O and N-H groupings in relation to the amide bond. This circumstance together with the presence of the above IHB excludes the possibility of the bifunctional mechanism of the amide bond participation in the formation of the cyclic transitional state of type I.

At the same time it is not excluded that the formation of IHB influences conjugation in the amide fragment. An increase the acceptor properties in R and R' substitutes may increase the degree of conjugation. We have found indications in the literature[39] that intramolecular solvation may influence the degree of conjugation in the amide fragment of N-acyl-amino acid esters. It is not excluded that intramolecular solvation as seen from II may be of equal importance.

Apparently it is due to the formation of such a cycle as reflected by II that the relatively high transmission of electron influence of R and R' (see ρ^* in equations 7 and 9) to the C=O amide group takes place, despite the considerable remoteness of these substituents. It has also been indicated (cf. ρ^* in equations 7 and 9) that the sensitivi-

ty is higher to substituent R' which is more remote from the C=O amide group but closely related to the atom of oxygen which takes part in IHB formation than the sensitivity to substituent R in the lateral part of the amino acid which stands closer to the catalytically active center, but more remote from the atoms which take part in IHB formation.

In the light of the above said the following experimental fact is of considerable interest. The direction of the induction influence of substituent R' in N,N-disubstituted amino acid esters (cf. Nos. 19 and 20) where IHB formation of type II is not possible, is contrary to what occurs in the corresponding N-monosubstituted derivatives (cf. Nos. 13 and 16). It once again confirms the determining role of IHB in the effectiveness and direction of the transmission of the electron effects of R and R' substituents to the catalytic activity of N-acylamino acid esters in the reaction of peptide bond formation.

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SOLVENT EFFECTS ON THE CONFORMATIONAL BALANCE OF α-CHLOROACETOPHENONE

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Infrared spectroscopy has been applied to study the conformational balance of α-chloroacetophenone in the gaseous phase and a large variety of organic solvents. A quantitative relationship revealing the influence of nonspecific and specific solvent properties on the state of conformer balance is established and discussed. The free conformational energy of α-chloroacetophenone is found to correlate only with the frequency of the C=O valence vibrations band of the cis form.

Research into the conformational structure of a variety of α-acetophenone halides has indicated that halogenalkyl groups occupy balanced gauche and cis positions in relation to the carbonyl group[1,2].

The infrared spectra of α-chloroacetophenone solution show it in the doublet splitting of the carbonyl absorption band, the low frequency component of which corresponds to the less polar gauche stereoform and the high frequency one to the more polar conformer with the cis orientation of C-Cl and C=O bonds[3].

Since the energy of isomeric transitions in solutions (ΔF_{obsd}) is determined[4] by the rhotamerization of isolated molecules (ΔF_0) as well as by various solvatation interactions ($\sum_i \Delta F_i$) in accordance with eq.(1) it was of interest

$$\Delta F_{obsd} = \Delta F_c + \sum_i \Delta F_i \qquad (1)$$

to consider the medium effects on its conformational balance on the example of α-chloroacetophenone. The present work is devoted to the solution of this task.

EXPERIMENTAL

As media we used pure cyclohexane, benzene and its derivatives, n-butyronitrile, 1,4-dioxane, 2-propanol and cyclohexanol as well as binary mixtures of cyclohexane with a variety of solvents. All the substances involved were purified by well-known methods[5]. Infrared spectra of α-chloroacetophenone in the given media (Table 1) were obtained on a UR-20 spectrophotometer in the frequency range 1640-1760 cm^{-1} *). At this the concentration of α-chloroacetophenone solutions was kept constant for all the cases and equalled 0.0400 M. In the gaseous phase the infrared spectra of α-chloroacetophenone were recorded at balanced concentrations, which corresponded to the elasticity of its pair at 30°C, the optical length of a beam run being 876 cm.

DISCUSSION AND RESULTS

The results obtained (Table 1) indicate that the conformational structure of α-chloroacetophenone is rather sensitive to medium changes. An increase in its polar properties, in particular, will lead to a relative increase in the cis form intensity (Fig.1).

The thermodynamic properties of carbonyl containing compounds rhotamerization are often determined on the basis of integral intensities of individual conformer bands (see, e.g. ref.7). However, in case these bands considerably overlap (Fig.1) any reliable determination of their integral intensities will prove to be impossible due to the errors which are creeping in at splitting the overall band

*) For further details about spectra recording conditions see ref. 6.

Table 1

Molar absorption coefficients of $\nu_{C=O}$ band of α-chloroacetophenone in individual solvents S and its binary mixtures with cyclohexane at various values of molar fractions N_S, at 30°C

No	N_S	$\varepsilon^{gauche}_{C=O}$ $M^{-1}\cdot cm^{-1}$	$\varepsilon^{cis}_{C=O}$ $M^{-1}\cdot cm^{-1}$	$\log \frac{\varepsilon^{cis}_{C=O}}{\varepsilon^{gauche}_{C=O}}$	No	N_S	$\varepsilon^{gauche}_{C=O}$ $M^{-1}\cdot cm^{-1}$	$\varepsilon^{cis}_{C=O}$ $M^{-1}\cdot cm^{-1}$	$\log \frac{\varepsilon^{cis}_{C=O}}{\varepsilon^{gauche}_{C=O}}$
1	2	3	4	5	1	2	3	4	5
I. Cyclohexane					**VI. 1,2,4-Trichlorobenzene**				
1	1.0000	226	133	-0.231	30	0.05026	219	132	-0.220
					31	0.1004	216	133	-0.211
II. Benzene					32	0.2286	218	162	-0.129
2	0.1091	231	148	-0.193	33	0.3502	215	175	-0.0894
3	0.2244	232	160	-0.161	34	0.5017	198	183	-0.0342
4	0.3515	233	178	-0.117	35	0.7510	178	182	0.00965
5	0.5029	228	187	-0.0861	36	1.0000	154	170	0.0429
6	0.6513	224	198	-0.0536					
7	0.8025	214	215	0.00203	**VII. Benzonitrile**				
8	1.0000	198	223	0.0523	37	0.05037	218	155	-0.148
					38	0.09805	211	175	-0.0812
III. Toluene					39	0.2254	193	197	0.00891
9	0.1008	219	146	-0.176	40	0.3495	180	211	0.0690
10	0.2226	220	162	-0.133	41	0.5028	156	229	0.167
11	0.3521	211	177	-0.0763	42	0.7453	137	230	0.225
12	0.4971	214	200	-0.0294	43	1.0000	124	219	0.247
13	0.6560	211	218	0.0142					
14	0.8013	198	209	0.0235	**VIII. n-Butyronitrile**				
15	1.0000	177	210	0.0733	44	0.04932	210	152	-0.140
					45	0.1002	207	171	-0.0830
IV. Chlorobenzene					46	0.2253	193	199	0.0133
16	0.04784	233	144	-0.209	47	0.3510	188	206	0.0397
17	0.08861	224	145	-0.189	48	0.5002	179	221	0.0915
18	0.2193	226	166	-0.134	49	0.7503	160	218	0.134
19	0.3523	222	185	-0.0792	50	1.0000	152	225	0.170
20	0.5028	216	200	-0.0334					
21	0.7529	192	196	0.00896	**IX. Nitrobenzene**				
22	1.0000	173	202	0.0674	51	0.02262	234	149	-0.196
					52	0.04960	229	158	-0.161
V. 1,2-Dichlorobenzene					53	0.1538	204	182	-0.0496
23	0.04496	234	148	-0.199	54	0.3353	191	213	0.0473
24	0.07500	230	145	-0.181	55	0.6561	152	207	0.134
25	0.2188	214	176	-0.0849	56	1.0000	139	229	0.217
26	0.3387	194	191	-0.00677					
27	0.4931	161	200	0.0942	**X. 1,2-Dimethylbenzene**				
28	0.7517	151	205	0.133	57	1.0000	166	201	0.0831
29	1.0000	151	226	0.175					

Table 1 (continued)

1	2	3	4	5	1	2	3	4	5
XI. 1,4-Dimethylbenzene					XV. Triethylamine				
58	1.0000	184	240	0.115	69	0.05005	211	132	-0.204
XII. Mesitylene					70	0.09924	215	138	-0.193
59	1.0000	207	174	-0.0754	71	0.1996	210	140	-0.176
XIII. 1,4-Dioxane					72	0.3508	202	143	-0.150
60	1.0000	165	229	0.142	73	0.5017	201	152	-0.121
XIV Diethyl ether					74	0.7010	185	147	-0.0999
61	0.1008	215	136	-0.199	75	1.0000	-	-	-0.0691*)
62	0.2293	211	145	-0.163	XVI. Pyridine				
63	0.3421	210	157	-0.126	76	0.03656	254	162	-0.195
64	0.5027	201	163	-0.0910	77	0.1752	212	178	-0.0759
65	0.6518	197	179	-0.0416	78	0.2832	208	202	-0.0127
66	0.8040	197	192	-0.0112	79	0.4192	187	210	0.0504
67	0.9017	190	199	0.0201	80	0.6491	146	212	0.162
68	1.0000	-	-	0.0294*)	81	1.0000	-	-	0.279*)
					XVII. Gaseous phase				
					82	-	-	-	-0.750**)

*) The data have been obtained by extrapolating dependences

$$\lg \frac{\varepsilon^{cis}_{C=O}}{\varepsilon^{gauche}_{C=O}} = f(N_s) \text{ into } N_s = 1.$$

**) The value calculated on the basis of optical transmissivities (T) in the peaks of the $\nu_{C=O}$ band.

into components. Besides, when proceeding to more polar aprotic solvents in α-chloroacetophenone spectra, the low frequency asymmetry of both components of the $\nu_{C=O}$ doublet is observed, on the other hand in the media of protic solvents, as a result of H-bond formation, each component is in its turn split into a doublet (Fig.2). This eliminates the possibility to obtain reliable values of integral intensities of the bands of individual rhotamer forms of α-chloroacetophenone.

Taking into account the above said as well as the fact that the peak intensities of $\nu_{C=O}$ bands appear to be considerably less sensitive to the asymmetry of the band contour

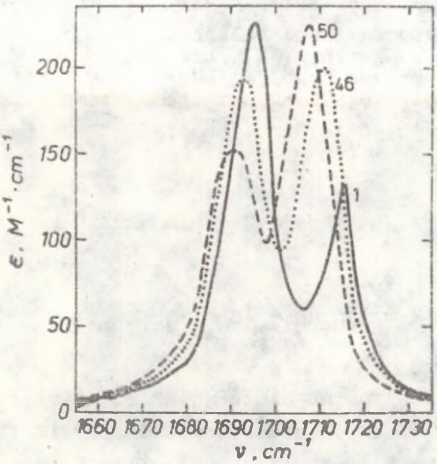

Fig.1. Contours of the C=O stretching vibrations band of α-chloroacetophenone in various solutions, at 30°C. The numbering corresponds to that of Table 1.

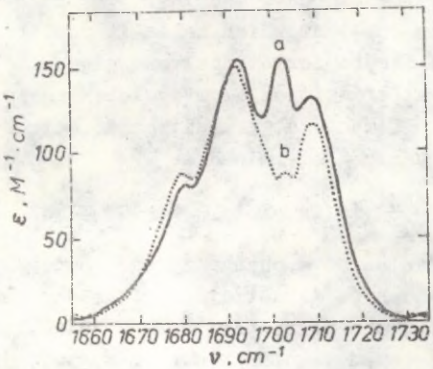

Fig.2. Contours of the C=O stretching vibrations band of α-chloroacetophenone in 2-propanol (a) and cyclohexanol (b), at 30°C.

due to intramolecular interactions than the integral intensities[6], molar absorption coefficients in the peaks of $\nu_{C=O}$ bands ($\varepsilon^{gauche}_{C=O}$ and $\varepsilon^{cis}_{C=O}$ $M^{-1}\cdot cm^{-1}$) were used to quantitatively describe the conformational balance.

Table 1 displays $\varepsilon^{gauche}_{C=O}$ and $\varepsilon^{cis}_{C=O}$ values as well as the logarithms of their relations for the systems studied.

It follows from the determination of $\varepsilon^{gauche}_{C=O}$ and $\varepsilon^{cis}_{C=O}$ that

$$\varepsilon^{gauche(cis)}_{C=O} = \varepsilon^{gauche(cis)}_{o} \frac{C_{gauche(cis)}}{C} ; \quad (2)$$

$$\lg \frac{\varepsilon^{cis}_{C=O}}{\varepsilon^{gauche}_{C=O}} = \lg \frac{\varepsilon^{cis}_{o}}{\varepsilon^{gauche}_{o}} + \lg K , \quad (3)$$

where $\varepsilon^{gauche(cis)}_{o}$ are the absolute molar coefficients of conformer absorption of α-chloroacetophenone, C is its analytical concentration, K is the constant of conformational transition. Rather insignificant (15-20%) changes in the sum of $\varepsilon^{gauche}_{C=O}$ and $\varepsilon^{cis}_{C=O}$ intensities and the symbaticity of $\nu^{gauche(cis)}_{C=O}$ frequencies enabled us to assume that when varying the medium, there will be a similar change in $\varepsilon^{gauche(cis)}_{o}$ values. In this case the $\lg \varepsilon^{cis}_{o} / \varepsilon^{gauche}_{o}$ value will remain nearly constant which makes it possible to assess the changes in the conformational energies of α-chloroacetophenone ($\Delta\Delta F$) at transition from cyclohexane to any of the solvents studied. Thus, at transition to nitrobenzene the $\Delta\Delta F$ value which can be determined as $RT \ln \frac{(\varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O})_{NB}}{(\varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O})_{CH}}$ is equal to $2.60 \cdot 10^{3}$ $J \cdot mol^{-1}$. The behavior of the $\Delta\Delta F$ value at a change in the composition of other studied systems can be illustrated by the dependence of $\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O}$ on the molar portion the solvent S (Fig.3) added to cyclohexane. An increase in the prominence of the given curves in the initial parts of the concentration axis when increasing the polar properties of the S component (Fig.3) could be possibly ascribed to the strengthe-

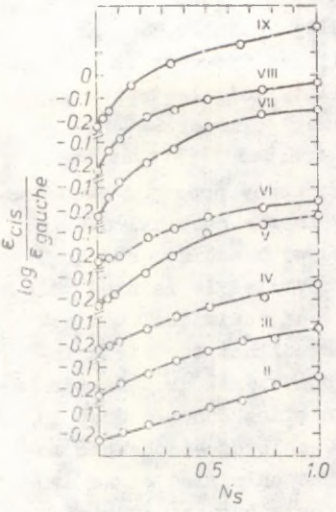

Fig.3. The dependence of $\lg \frac{\varepsilon_{cis}}{\varepsilon_{gauche}}$ on the composition of the solvent, at 30°C. Curve numbers correspond to those in Table 1.

ning of selective solvatation of α-chloroacetophenone by the molecules of S.

To quantitatively estimate the influence of medium on the conformational balance of α-chloroacetophenone we have applied an equation which additionally takes into account the nonspecific and specific properties of solvents[8]:

$$\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O} = \left(\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O}\right)_o + yY + pP + bB + eE, \quad (4)$$

where $\left(\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O}\right)_o$ is the value of $\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O}$ in the gaseous phase; $Y = \frac{\varepsilon - 1}{\varepsilon + 2}$ and $P = \frac{n^2 - 1}{n^2 + 2}$ are the functions of polarity and polarizability; B and E denote general basicity[9] and acidity[10] parameters; y, p, b and e denote the sensitivity of conformational free energies of α-chloroacetophenone to changes in these properties of solvents. The values for regression coefficients in eq.(4) were calculated by the least squares method[11] on a "Mir-1" computer. For solvents Nos. 1,8,15,22,29,43,56,59,60,68,75 and 81 the following numerical solution of eq.(4) was obtained:

$$\lg \varepsilon^{cis}_{C=O} / \varepsilon^{gauche}_{C=O} = -(5.76 \pm 1.82) \cdot 10^{-1} + (5.62 \pm 0.89) \cdot 10^{-1} Y + (9.77 \pm 6.93) \cdot 10^{-1} P + (1.85 \pm 0.92) \cdot 10^{-4} B + (7.00 \pm 1.40) \cdot 10^{-2} E, \quad (5)$$

$$S = 0.0507\ (9.9\%),\ R = 0.963,\ n = 12.$$

The comparison of the free member of the obtained rela-

tionship with the value -0.750 obtained from the infrared spectra of α-chloroacetophenone in pairs (Table 1) shows that relationship (5) is statistically reliable.

We have shown earlier[6] that with an increase in solvent polarity, polarizability, nucleophility and electrophility the $\nu_{C=O}$ bands of individual rhotamer forms of α-chloroacetophenone displace into the low frequency part. At the same time a decrease in the $\nu^{cis}_{C=O}$ frequency proceeds much faster. It can be seen that a decrease in the carbonyl doublet frequencies of α-chloroacetophenone with an increase in nonspecific and specific solvent properties is related to a decrease in orders of carbonyl bonds of individual conformers. In this case it might be expected that the field interaction between the C=O and C-Cl bonds will drop faster in the cis conformer which is likely to bring about a drop in the conformational free energy of α-chloroacetophenone molecules. In fact, relationship (5) has only plus signs at the members which characterize the contributions of various solvent properties at disturbing the rhotamer balance of α-chloroacetophenone towards the cis form.

Besides, we have observed how the state of conformer balance is directly influenced by the carbonyl bond orders of individual conformers of α-chloroacetophenone. With this aim in view the values of $\lg \varepsilon^{cis}_{C=O}/\varepsilon^{gauche}_{C=O}$ (Table 1) were correlated with the frequencies in the peaks of $\nu_{C=O}$ bands. The following relationship was obtained:

$$\lg \varepsilon^{cis}_{C=O}/\varepsilon^{gauche}_{C=O} = (6.36\pm1.57)\cdot10^{-1} + (1.18\pm1.17)\cdot10^{-2}\times$$
$$\times(\nu^{gauche}_{C=O} - 1700) - (4.98\pm0.63)\cdot10^{-2}(\nu^{cis}_{C=O} - 1700), \quad (6)$$
$$S = 0.0415\ (8.14\%),\ R = 0.948,\ n = 81.$$

If we apply the frequency values obtained from the spectra of pairs of α-chloroacetophenone[6] to eq.(6) we get the value $\lg \varepsilon^{cis}_{C=O}/\varepsilon^{gauche}_{C=O}$ equal to -0.755±0.448 which is in agreement with the experimental value -0.750.

Equation (6) shows that the free conformational energy of α-chloroacetophenone does not depend on the frequen-

cies of C=O stretching vibrations of the gauche form and correlates only with the frequencies of the carbonyl absorption of the cis form. In fact, the reciprocal orientation of the carbonyl and halogenmethyl fragments of a molecule in the cis form to the peak field interaction of C=O and C-Cl bonds. At this an increase in the order of the cis conformer carbonyl bond is likely to favour an increase in the repulsive interactions between the given fragments of molecules as well as a shift of the conformer balance towards the gauche form. As a result of this the sensitivity of $\lg \varepsilon^{cis}_{c=o} / \varepsilon^{gauche}_{c=o}$ to a change in the $\nu_{c=o}$ frequency of the cis conformer in relationship (6) is negative in sign.

Thus, the results obtained in the present work indicate that the conformational structure of α-chloroacetophenone is to a considerable degree determined by the nature of its intramolecular interactions with the molecules of the solvent. At the same time an increase in nonspecific as well as specific solvent properties shifts the conformational balance towards the formation of the cis form. It has also been shown that the free energy of the conformational transition of α-chloroacetophenone correlates with the frequencies of carbonyl absorption of cis conformers.

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KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES. XII HYDROLYSIS OF TOSYLATES WITH ELECTRONEUTRAL SUBSTITUENTS IN THE PRESENCE OF NaCl AND $NaClO_4$

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The kinetics of alkaline hydrolysis of eight substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X with electroneutral substituents (X = 4-NO_2, 3-NO_2, 3-NH_2, 4-NH_2, 3-CH_3, 2-NO_2, 2-NH_2, 2-OCH_3) as dependent on the concentrations of additions of neutral electrolyte NaCl as well as of three phenyl tosylates (X=4-NH_2, 2-OCH_3, 2-NH_2) dependent on $NaClO_4$ concentrations has been studied at 75°C. In the presence of NaCl only small positive salt effects were detected, their values increasing with a decrease in the rate of reaction.

The values of electrophilicity parameters (E) for concentrated aqueous solutions of NaCl and $NaClO_4$ ($\sqrt{\mu}$ =2.3) as well as for 7.75 molal solution of Bu_4NBr were calculated.

When studying the salt effects on interionic reactions with a charged substituent substrate, the values of salt effects for the same charged substituent were found to be dependent on both the reaction considered and the nature of the added neutral electrolyte[1-11].

The gross salt effect for compounds with charged substituents was assumed to consist of electrostatic $\Delta \log k_{el}$

and specific $\Delta \log k_{sp}$ components.[12] In the case of electroneutral substituents the salt effects were assumed to characterize changes in the intensity of specific solvation with transition from pure water to salt solution. Subtracting the contribution of specific solvation from the overall salt effect, one can obtain the values of salt effects of purely electrostatic character for charged substituents.

In order to compare the values of electrostatic components for the charged substituents found from the data for the alkaline hydrolysis of substituted phenyl benzoates and phenyl tosylates in the presence of NaCl and $NaClO_4$ additions it seems expedient to study in detail how the values of salt effects of substrates with electroneutral substituents depend on the nature of the latter as well as on the added neutral electrolyte.

Our previous papers [12-15] were devoted to the influence of $NaClO_4$ and NaCl on the alkaline hydrolysis of substituted phenyl and alkyl benzoates as well as to the alkaline hydrolysis of substituted phenyl tosylates in the presence of $NaClO_4$ additions in the case of electroneutral substituents.

The present communication reports the data on the kinetics of the alkaline hydrolysis of eight phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X (X = 4-NO_2, 3-NO_2, 4-NH_2, 3-NH_2, 3-CH_3, 2-NO_2, 2-NH_2, 2-OCH_3) in the presence of NaCl and for three phenyl tosylates (X = 4-NH_2, 2-OCH_3, 2-NH_2) in the presence of $NaClO_4$ at 75°C.

Experimental

Preparation and characteristics of the substituted phenyl tosylates and the technique of kinetic measurements are described in Refs. 16 and 17.

Kinetic measurements were carried out under pseudomonomolecular conditions with a high alkali excess. The second order rate constants k_2 were calculated by dividing pseudo-first order rate constants k_1 by the alkali concentration. The measurements at each ionic strength were repeated 2-6

Table 1

Rate Constants of Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X in the Presence of NaCl and $NaClO_4$ at 75°C

X	$10^3 C_{NaOH}$ (M)	C_{salt} (M)	$10^2.k_2$ ($M^{-1}.sec^{-1}$)	n*	λ ** (nm)
1	2	3	4	5	6
		Additions of NaCl			
4-NO_2	4.44	-	21.6±0.3	4	410
	4.44	1.00	20.5±0.8	2	
	4.44	4.00	21.8±1.6	2	
	4.44	4.84	21.2±1.2	4	
3-NO_2	4.44; 11.1	-	14.5±0.8	4	250
	4.04	1.00	14.9±0.7	2	
	4.04;4.44	4.00	18.2±1.6	5	
	4.44	4.84	18.9±1.8	3	
3-CH_3	44.4; 111 326	-	0.613±0.028	13	245
	44.4	3.24	0.788±0.014	3	
	44.4	4.00	0.877±0.087	6	
	44.4	4.84	0.653±0.016	1	
3-NH_2	40.4;101	-	0.483±0.022	7	236
	40.4	1.00	0.417±0.010	4	
	40.4	4.00	0.779±0.023	4	
	40.4	4.84	0.752±0.107	2	
4-NH_2	44.4;101	-	0.211±0.004	6	236
	40.4;44.4	1.00	0.271±0.021	2	
	40.4;44.4	4.00	0.324±0.019	6	
	44.4	4.84	0.377±0.014	3	

Table 1 (continued)

1	2	3	4	5	6
2-NO_2	2.02	-	70.1±2.6	4	410
	2.02	1.00	79.4±2.9	2	
	2.02	4.00	73.1±8.3	2	
	2.02;4.04	4.84	64.9±2.5	6	
2-OCH_3	20.2;101	-	0.765±0.035	8	245
	20.2	1.00	1.01 ±0.06	2	
	20.2	3.24	1.63 ±0.07	4	
	20.2	4.00	1.49 ±0.08	9	
2-NH_2	20.2;101	-	1.06 ±0.02	7	240
	20.2	1.00	0.895±0.120	2	
	20.2	4.00	1.52 ±0.04	3	
	20.2	4.84	1.64 ±0.08	4	
			Additions of $NaClO_4$		
4-NH_2	40.0	5.29	0.138±0.014	3	236
2-OCH_3	20.0;40.0	5.29	0.710±0.020	3	245
2-NH_2	20.0;40.0	5.29	0.709±0.071	3	240

* - Number of measurements at the salt concentration considered.

** λ - Wavelengths used at measurements

times and the arithmetic means of the corresponding second order rate constants k_2 were calculated.

The values of k_2 (M^{-1} sec^{-1}) for the alkaline hydrolysis of eight substituted phenyl tosylates at various concentrations of NaCl as well as for three phenyl tosylates at the concentration of $NaClO_4$ 5,29 ($\sqrt{\mu}$ =2.3) are given in Table 1.

The number of parallel measurements at each salt concentration and the wavelengths used are given in Table 1 as well.

In Fig. 1 one can see the dependences of log k on $\sqrt{\mu}$ (μ -ionic strength) for the alkaline hydrolysis of substituted phenyl tosylates in the presence of NaCl.

Discussion

The values of salt effects

$$\Delta \log k^x_{js} = \log k^x_{js} - \log k^x_{jo} \qquad (1)$$

for the alkaline hydrolysis of substituted phenyl tosylates in the presence of NaCl and $NaClO_4$ are given in Table 2. k_{js} is the rate constant in the presence of neutral salt and k_{jo} is the rate constant at zero concentration of an added salt. Indices x and j denote the substituent and reaction series, respectively.

For 4-NO_2- and 2-NO_2-phenyl tosylates no dependence of the rate constant on the added NaCl concentration was observed. In the case of all other phenyl tosylates (3-NO_2, 3-CH_3, 3-NH_2, 4-NH_2, 2-NH_2, 2-OCH_3) in the presence of NaCl relatively low positive salt effects were observed. It is interesting to note that a considerable increase in the rate constant was detected only at high NaCl concentrations ($C_{NaCl} > 1$). Low concentrations of NaCl practically do not influence the rate constant (see Fig.1).

The values of these salt effects $\Delta \log k^x_{js}$ linearly depend on $\log k^x_{jo}$ (see Fig.2 and 3):

$$\Delta \log k^x_{js} = a_{js} \log k^x_{jo} + b_s \qquad (2)$$

or

$$\log k^x_{js} = (a_{js} + 1) \log k^x_{jo} + b_s \qquad (3)$$

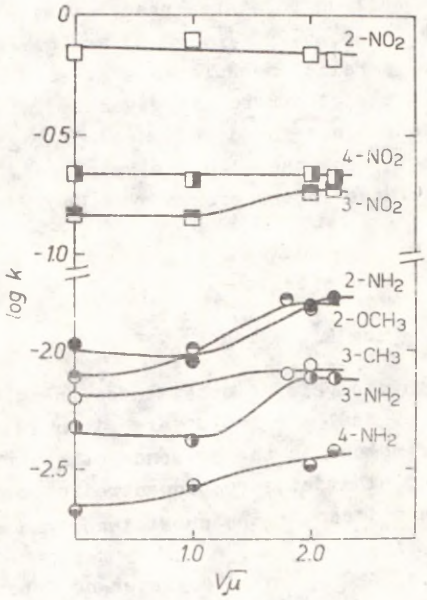

Fig. 1. The dependence of log k on $\sqrt{\mu}$ for alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4 - X$ in the presence of NaCl at 75°C.

Table 2

Values of $\log k^X_{jo}$, $\log k^X_{js}$ and $\Delta \log k^X_{js}$ = $= \log k^X_{js} - \log k^X_{jo}$ for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4 - X$ in the Presence of NaCl and $NaClO_4$ at 75°C

X	$\log k^X_{jo}$	$\sqrt{\mu}$(NaCl)=2.2		$\sqrt{\mu}$(NaCl)=2.0 and 2.2*	
		$\log k^X_{js}$	$\Delta \log k^X_{js}$	$\log k^X_{js}$	$\Delta \log k^X_{js}$
4-NO_2	-0.666	-0.674	-0.008	-0.670	-0.004
3-NO_2	-0.839	-0.724	0.115	-0.733	0.106
3-CH_3	-2.213	-2.073	0.140	-2.082	0.131
3-NH_2	-2.317	-2.124	0.193	-2.114	0.203
4-NH_2	-2.676	-2.424	0.252	-2.466	0.210
2-NO_2	-0.154	-0.188	-0.034	-0.175	-0.021
2-NH_2	-1.975	-1.785	0.190	-1.799	0.176
2-OCH_3	-2.116	-1.837	0.289	-1.818	0.298
		$\sqrt{\mu}(NaClO_4)$ = 2.3			
4-NH_2	-2.676	-2.860	-0.184		
2-OCH_3	-2.116	-2.149	-0.033		
2-NH_2	-1.975	-2.149	-0.175		

* Value of $\log k^X_{js}$ is the averaged value of $\log k^X_{js}$ at $\sqrt{\mu}$=2.0 and $\sqrt{\mu}$=2.2

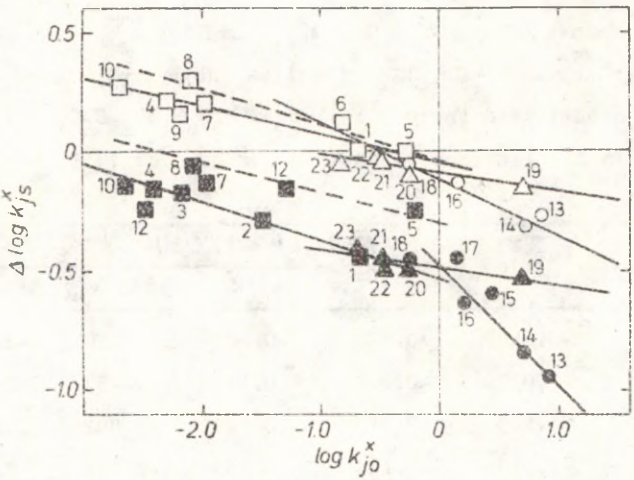

Fig. 2. The dependence of $\Delta\log k^X_{js} = \log k^X_{js} - \log k^X_{jo}$ on $\log k^X_{jo}$.

Notation of points:

Light points - with addition of NaCl ($\sqrt{\mu}$ =2.2)

Shaded points - with addition of $NaClO_4$ ($\sqrt{\mu}$ =2.3).

1. $CH_3C_6H_4SO_2OC_6H_4$-X + OH^-, 75°C (□, ■)

1. 4-NO_2; 2.3-Cl; 3.H; 4.3-NH_2; 5.2-NO_2; 6.3-NO_2; 7.2-NH_2; 8.2-OCH_3; 9.3-CH_3; 10.4-NH_2; 11.2-F; 12.2-CH_3.

2. $C_6H_5COOC_6H_4$ - X + OH^-, 50°C (○, ●)

13.4-NO_2; 14.2-NO_2; 15.2-F; 16.H; 17.3-NH_2; 18.2-CH_3.

3. C_6H_5COO - X + OH^-, 50°C (△, ▲)

19.CH_2Cl; 20.CH_2CH_2Cl; 21.$CH_2CH_2OCH_3$; 22.CH_3; 23.CH_2CH_3.

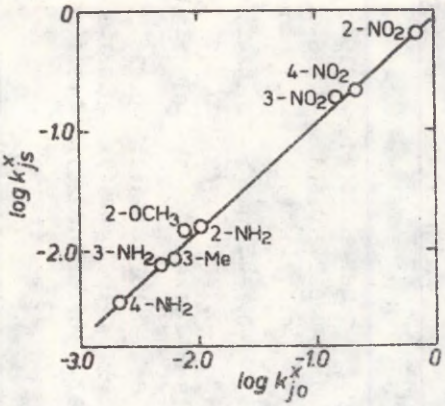

Fig. 3. The dependence of log k^X_{js} on log k^X_{jo} for alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in the presence of NaCl ($\sqrt{\mu}$ = 2.2), at 75°C.

The results of data treatment according to equations (2) and (3) are displayed in Table 3.

Relationships between log k values and σ° constants for alkaline hydrolysis of substituted phenyl tosylates in water, and in concentrated aqueous solutions of NaCl($\sqrt{\mu}$ = 2.2) and $NaClO_4$ ($\sqrt{\mu}$ =2.3) at 75°C can be described as follows:

$$\log k_{H_2O} = (-2.066 \pm 0.004) + (1.719 \pm 0.024)\sigma^\circ$$

$$s = 0.026 \qquad r = 0.9995$$

$$\log k_{(NaCl_{aq})} = (-1.922 \pm 0.017) + (1.577 \pm 0.091)\sigma^\circ$$

$$s = 0.097 \qquad r = 0.992$$

Table 3

Values of a and b for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X at 75°C in the Presence of NaCl

Substituents X	$\sqrt{\mu}$(NaCl)=2.2 a*	b	n**	$\sqrt{\mu}$(NaCl)=2.0 and 2.2*** a*	b	n**
1. 4-NO_2,3-NO_2,	-0.093±0.029(2)	-0.024±0.072	5	-0.082±0.026(2)	-0.016±0.066	5
3-CH_3,3-NH_2,	-0.093±0.029(3)	-0.024±0.072	5	-0.082±0.026(3)	-0.016±0.066	5
4-NH_2	-0.089±0.025(3)	-0.034±0.096	19	-0.077±0.015(3)	-0.010±0.080	39
2. 2-NO_2,2-NH_2,	-0.161±0.008(2)	-0.059±0.016	3	-0.139±0.047(2)	-0.046±0.098	3
2-OCH_3	-0.147±0.035(3)	-0.061±0.074	3	-0.140±0.047(3)	-0.047±0.098	3
	-0.155±0.017(3)	-0.063±0.068	18	-0.148±0.015(3)	-0.051±0.072	28
3. 4-NO_2,3-NO_2,	-0.110±0.023(2)	-0.037±0.068	8	-0.101±0.025(2)	-0.026±0.073	8
3-CH_3,3-NH_2,	-0.110±0.023(3)	-0.027±0.073	8	-0.100±0.025(3)	-0.027±0.073	8
4-NH_2,2-NO_2,	-0.095±0.008(3)	-0.010±0.040	37	-0.102±0.012(3)	-0.024±0.088	67
2-NH_2,2-OCH_3						

* Equation by which the values of "a" and "b" were calculated is given in parentheses.

** Number of data involved in regression data processing. According to equation (3) the data treatment was carried out by two different ways: either the arithmetic means of log k_2 values or log k_2 values for all parallel measurement were involved.

*** When calculating "a" and "b" values log k_2 at $\sqrt{\mu}$= 2.0 and $\sqrt{\mu}$=2.2 were embraced.

$$\log k_{(NaClO_4 aq)} = (-2.347 \pm 0.091) + (1.283 \pm 0.116)\,\delta^{\circ}$$

$$s = 0.081 \qquad r = 0.983$$

In the data processing the "recommended" values of δ° from Tables [18] were used.

Passing from water to the concentrated aqueous solution of NaCl ($\sqrt{\mu}$=2.2) the ρ° value decreases less than when passing from water to a similar solution of $NaClO_4$ ($\sqrt{\mu}$=2.3) with the same salt concentration.

In one of our previous works[19] it was found that

$$\rho^{\circ}_{js} - \rho_{j(H_2O)} = (-0.0842 \pm 0.0056)(E_s - E_{H_2O}) \qquad (4)$$

where E_s and E_{H_2O} - are electrophilicity parameters of the given medium and water[20,21].

A decrease in the $\rho^{\circ}_{js_o}$ value in comparison with water i.e. the negative $\rho^{\circ}_{js} - \rho_{j(H_2O)}$ value as well as the negative a_{js} value indicate that the electrophilicity of such a medium is higher than that of water. For aqueous salt solutions such a conclusion agrees fairly well with our expectations. For example, the value of electrophilicity parameter E for 4.5 molar aqueous solution of LiCl has been found equal to 28.4[22].

According tc equation (4) we calculated the values of electrophilicity parameters for concentrated aqueous solution of NaCl ($\sqrt{\mu}$=2.2, E = 24.0) and $NaClO_4$ ($\sqrt{\mu}$=2.3, E = 26.6) as well as for 7.75 molal aqueous solution of n-Bu_4NBr(E=9.8).

When calculating E values the averaged differences ($\rho^{\circ}_s - \rho^{\circ}_o$) were used, the latter having been found from the relationship between a_{js} and $^1/\rho_{jo}$ (Fig.4) for alkaline hydrolysis of substituted phenyl benzoates, alkyl benzoates and phenyl tosylates according to equation[14]:

$$a_{js}\rho_{jo} = \rho_s - \rho_o \qquad (5)$$

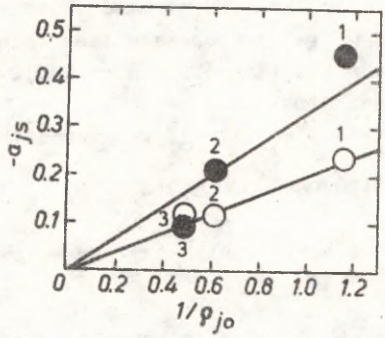

Fig. 4. The dependence of a_{js} on $1/\rho_{jo}$.
1. $C_6H_5COOC_6H_4$-X + OH^- , 50°C
2. $CH_3C_6H_4SO_2OC_6H_4$-X + OH^- , 75°C
3. C_6H_5COO-X + OH^-, 50°C

Light points - with addition of NaCl($\sqrt{\mu}$=2.2)
Shaded points - with addition of $NaClO_4$($\sqrt{\mu}$=2.3)

For aqueous solution of NaCl($\sqrt{\mu}$=2.2) we found

$$\rho_s^o - \rho_o^o = -0.187 \pm 0.014$$

and for aqueous solution of $NaClO_4$ ($\sqrt{\mu}$=2.3):

$$\rho_s^o - \rho_o^o = -0.404 \pm 0.053$$

When calculating the E values for 7.75 molal aqueous solution of Bu_4NBr the average value $\rho_s^o - \rho_o^o = 1.03$ from publication[23] was used.

Addition of $NaClO_4$ to water causes an increase in the electrophilicity of medium more than in the case of NaCl.

At the same time addition of n-Bu_4NBr to water causes a decrease in the electrophilicity of medium and the electrophilicity parameter value for 7.75 molal aqueous solution of Bu_4NBr is comparable with such a parameter for 85% aqueous dimethyl sulfoxide.

It is interesting to mention that an analogous conclusion could be drawn from the data of salt effects for solvolysis of triphenylchlormethane in the presence of different salts[24-26]. It was found that when compared to chlorides with small cations the addition of perchlorates considerably increases but the addition of Bu_4NCl decreases the rate of solvolysis.

The detected order of electrophilicity parameters in concentrated aqueous solutions of NaCl, $NaClO_4$ and n-Bu_4NBr could be explained first of all in terms of the structure model for aqueous solutions of electrolytes. As for their behavior in relation to pure liquid water Frank and Evans divide ions into structure-breaking and structure-making.[27-32] Addition of mineral salts to water breaks the hydrogen bonds in water thus it increases the ability of water to form hydrogen bonds with other solutes. Among water structure-breaking ions the perchlorate ion rates one of the strongest[30].

The nature of the interaction of Bu_4N^+ ions with water molecules in solution is totally different from a such between water molecules and inorganic salts[27-32]. Bu_4N^+ ions stabilize the structure of water an increase the number of hydrogen bonds. The electrophilicity of such an aqueous medium is considerably lower than that of pure water.

The value of b_s found from the data of alkaline hydrolysis of phenyl tosylates in the concentrated aqueous solution of NaCl ($\sqrt{\mu}$=2.2) is practically as large as it has been found from the data of alkaline hydrolysis of phenyl benzoates and alkyl benzoates in the same medium[14] (see Table 3, Fig.3).

It should be mentioned that the b_s value turned out to be constant for the given medium also both when studying the alkaline hydrolysis of phenyl tosylates, and phenyl and

alkyl benzoates in the concentrated aqueous solution of $NaClO_4$ [14] as well as pK_a values of carboxylic acides, phenols, and amines in 7.75 molal solution of Bu_4NBr.

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KINETIC STUDY OF HYDROLYSIS OF BENZOATES. XV. ALKALINE HYDROLYSIS OF o-OH-PHENYL BENZOATE.

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The kinetics of alkaline hydrolysis of o-OH-phenyl benzoate dependent on the concentrations of NaOH as well as on additions of neutral electrolytes NaCl and $NaClO_4$ has been studied at different temperatures in water.

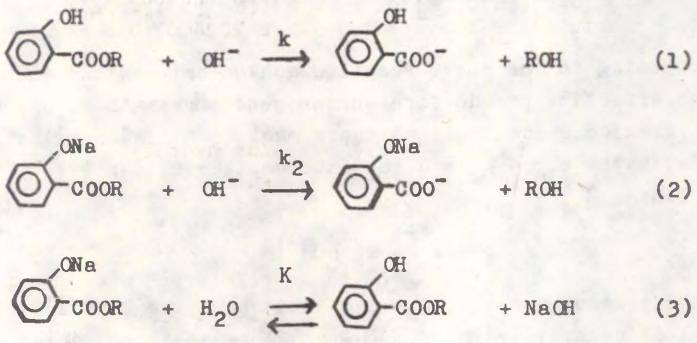
It was found that at low NaOH concentrations both acidic and anionic forms of o-OH-phenyl benzoates are involved. At higher NaOH concentrations and in the presence of a neutral electrolyte positive salt effects were observed.

The present work continues the systematic study of the alkaline hydrolysis salt effects of benzoates and tosylates.

One of our first papers[1] in this series reported the data about the influence of NaOH and NaCl concentrations on the kinetics of the alkaline hydrolysis of o-OH-phenyl tosylate. In this work we could not observe any dependence of the rate constant on either NaOH concentrations or additions of the neutral electrolyte NaCl in the concentration range studied. However, when applying later the differential-conductometric method[2] it was found that $o\text{-}O^-$ - phenyl tosylate in the NaOH solutions studied is almost completely in the state of ion pairs.

L. Pekkarinen and E. Tommila[3] have studied the alkaline hydrolysis of alkyl salicylates dependent on both hydroxide concentrations and additions of neutral electrolyte in pure

water and in the mixtures of water with different alcohols. These authors came to the conclusion that the above hydrolysis reaction involves both acidic and anionic forms of salicylate, which are in equilibrium with each other:



(1)

(2)

(3)

The total rate equation can be represented as follows[3]:

$$\frac{dx}{dt} = (k_1' + k_2 [OH^-]) (a - x) \qquad (4)$$

where $k_1' = kK$

k is the second-order rate constant for the alkaline hydrolysis of OH-form of salicylate;

k_2 is the same constant for an anionic form of salicylate,

a is the initial and

a-x the current concentrations of calicylate.

$$K = \frac{[C_6H_4(OH)COOR]\,[OH^-]}{[C_6H_4(ONa).COOR]\,.\,[H_2O]} = \frac{\xi(b + \xi - \eta)}{a - x - \xi}$$

where b is the initial concentration of alkali hydroxide;
ξ is the concentration of the salicylate OH-form;
η is the concentration of $C_6H_4(ONa)COONa$.

Taking into account that $\xi \ll a - x$ one can write:

$$k\left[C_6H_4(OH)COOR\right]\left[OH^-\right] = k\xi(b+\xi-\eta)=k.K(a-x)$$

According to the above reaction scheme between the values of the effective pseudo first-order rate constants k_1 and the hydroxide concentrations there must be a linear relationship with the slope k_2 and the intercept being equal to $k_1' = k.K$:

$$k_1 = k_1' + k_2\left[OH^-\right] \qquad (5)$$

The present work reports the data about the kinetics of the alkaline hydrolysis of o-OH-phenyl benzoate as dependent on both NaOH concentrations and additions of neutral electrolytes NaCl and $NaClO_4$.

On the one hand the applicability of the Pekkarinen and Tommila reaction scheme was checked, on the other hand it was interesting to learn how the additions of neutral electrolytes influence the rate of this reaction.

Experimental

o-Hydroxyphenyl benzoate was synthesized from pyrocatechol ("Chemapol" , grade "Pure") and benzoyl chloride ("Reanal", grade "Chemically Pure"). The product was recrystallized from water, m.p. 133-134°C (lit.value 130 - - 131°C[4]).

Found: C, 72.6; H, 4.58; O, 24.59.
Calculated: C, 72.8; H, 4,67; O, 22.4.

The kinetics of the alkaline hydrolysis of o-OH-phenyl benzoate was investigated as dependent on both NaOH concentrations and additions of NaCl at 15, 25, 40 and 50°C as well as additions of $NaClO_4$ at 50°C.

For the technique of kinetic measurements see Ref. 5.

The kinetic measurements were carried out under pseudo-monomolecular conditions on a spectrophotometer SF - 4A equipped with a photoelectric multiplier and a recorder of type LP mainly on the wave length 234 nm. For comparison some measurements were carried out on the wave lengths 260 nm and 320 nm (see Fig. 1).

It should be noted that the optical density at 234 nm is characteristic of the acyl part of benzoate and the change in the optical density at 234 nm corresponds to a decrease in the total concentration of benzoate in the course of reaction. It was found[6,7] that the peak optical density at 260 nm corresponds to the un-ionized form of pyrocatechol, the peak at 320 nm corresponds to the two ionized form and the one at 290-300 nm corresponds to the peak of the one-ionized form of pyrocatechol.

The optical densities measured at 260 and 320 nm could not reflect the course of the summary reaction since the different pyrocatechol forms are in equilibrium with each other:

$$C_6H_4(OH)_2 \overset{K_1}{\rightleftharpoons} C_6H_4(OH)O^- \overset{K_2}{\rightleftharpoons} C_6H_4(O^-)_2$$

Because of this the rate constants obtained by changes in the intensities of optical densities at 234, 260 and 320 nm could not coinside with each other (see Table 1).

The measurements at each NaOH concentration and addition of neutral electrolyte were repeated 2-6 times and the arithmetic means of the corresponding rate constants were calculated. The second order rate constants (k_{II}) were obtained by dividing rate constants of the pseudomonomolecular reaction by the alkali concentration.

The values of rate constants measured at various concen-

trations of NaOH and in the presence of NaCl and $NaClO_4$ additions are listed in Table 1. The number of parallel measurements at each NaOH and neutral electrolyte concentration is given in Table 1 as well.

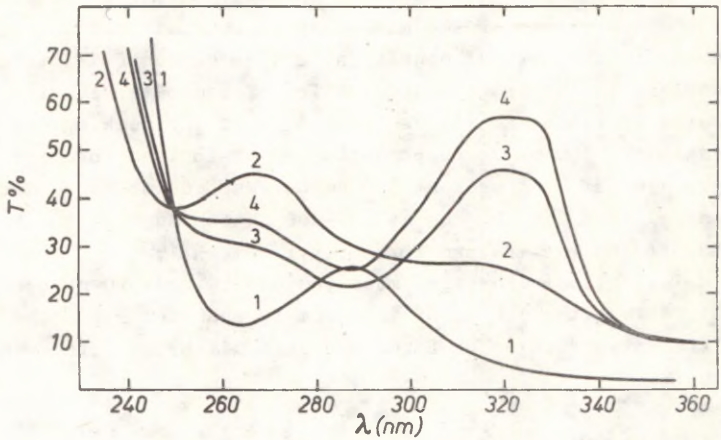


Fig. 1. Spectra of o-OH-phenyl benzoate

1. before hydrolysis in 0.01 M NaOH solution;
2. after hydrolysis in 0.01 M NaOH solution;
3. after hydrolysis in 0.1 M NaOH solution;
4. after hydrolysis in 0.4 NaOH solution.

Table 1

Rate Constants for Alkaline Hydrolysis of o-OH-Phenyl Benzoate at Various Concentrations of NaOH, NaCl and $NaClO_4$. (Mean square error of arithmetic mean is given for k). λ = 234 nm

C_{NaOH} (M)	C_{Salt} M	$10^3 . k_I$ (sec^{-1})	$10^2 . k_{II}$ ($M^{-1} . sec^{-1}$)	n*
1	2	3	4	5
		Additions of NaCl 15°C		
0.0825	-	0.561±0.007	0.680±0.009	3
0.104	-	0.660±0.027	0.635±0.025	3
0.132	-	0.837±0.035	0.634±0.027	4
0.208	-	0.983±0.022	0.472±0.011	5
0.333	-	1.37 ±0.04	0.411±0.013	3
0.412	-	1.66 ±0.02	0.403±0.005	4
0.659	-	2.59 ±0.01	0.393±0.002	4
0.825	-	3.39 ±0.07	0.410±0.008	4
1.51	-	8.64 ±0.13	0.572±0.008	2
1.51	3.24	13.7 ±0.3	0.909±0.022	5
1.53	2.56	13.9 ±0.4	0.909±0.026	2
1.65	3.19	14.3 ±0.2	0.865±0.010	5
1.66	-	8.91 ±0.10	0.537±0.006	4
1.69	-	8.93 ±0.05	0.528±0.003	4
1.69	2.31	13.5 ±0.1	0.796±0.007	5
1.69	3.15	15.4 ±0.1	0.909±0.006	5
3.07	-	28.3 ±1.3	0.926±0.039	4
		25°C		
0.0111	-	1.06 ±0.03	9.49 ±0.32	6
0.0111	0.100	1.01 ±0.11	9.10 ±0.10	2
0.0111	0.427	1.08 ±0.19	9.73 ±0.17	2
0.0111	1.80	1.05 ±0.06	9.46 ±0.05	2
0.0111	3.80	1.05 ±0.05	9.46 ±0.05	2
0.0111**	-	1.62 ±0.13	4.60 ±0.11	3

Table 1 (continued)

1	2	3	4	5
0.0111***	-	0.645±0.033	5.86 ±0.030	2
0.0394	-	1.33 ±0.04	3.37 ±0.09	4
0.0797	-	1.70 ±0.01	2.12 ±0.01	4
0.110	-	1.81 ±0.03	1.67 ±0.03	4
0.110**	-	2.59 ±0.11	2.35 ±0.10	3
0.110***	-	2.01 ±0.01	1.81 ±0.01	2
0.160	-	2.17 ±0.02	1.36 ±0.02	3
0.364	-	3.68 ±0.04	1.01 ±0.01	4
0.411	-	4.08 ±0.07	0.992±0.017	2
0.411**	-	4.72 ±0.21	1.15 ±0.05	3
0.411***	-	2.23 ±0.11	0.551±0.029	3
0.545	-	5.02 ±0.04	0.921±0.007	4
0.798	-	7.18 ±0.05	0.900±0.006	4
0.829	-	7.05 ±0.03	0.851±0.003	3
0.912	-	8.46 ±0.17	0.927±0.018	5
1.51	-	14.8 ±0.3	0.980±0.017	3
1.51	3.24	28.8 ±0.7	1.90 ±0.05	3
1.53	1.64	27.3 ±0.1	1.78 ±0.01	3
1.60	-	18.4 ±0.2	1.15 ±0.02	5
1.66	-	17.6 ±0.1	1.06 ±0.01	2
1.82	3.34	37.5 ±1.0	2.06 ±0.05	4
3.07	-	55.6 ±1.1	1.81 ±0.04	3
		40°C		
0.0109	-	4.75 ±0.10	43.6 ±0.9	5
0.0361	-	4.40 ±0.15	12.2 ±0.4	5
0.0544	-	4.55 ±0.07	8.36 ±0.13	5
0.0912	-	5.92 ±0.06	6.49 ±0.07	5
0.109	-	6.09 ±0.12	5.59 ±0.11	5
0.132	-	6.10 ±0.10	4.62 ±0.08	3
0.181	-	7.57 ±0.26	4.18 ±0.14	3
0.240	-	8.54 ±0.27	3.56 ±0.11	5
0.308	4.54	16.2 ±0.3	5.31 ±0.06	5

Table 1 (continued)

1	2	3	4	5
0.320	-	10.3 ±0.1	3.23±0.03	3
0.330	-	10.6 ±0.5	3.20±0.14	5
0.455	-	12.9 ±0.4	2.84±0.09	5
0.542	-	16.1 ±0.3	2.97±0.05	3
0.616	1.92	23.2 ±0.2	3.76±0.04	4
0.639	-	19.5 ±0.3	3.04±0.05	3
0.640	-	17.2 ±0.4	2.69±0.06	4
0.640	3.36	27.3 ±0.5	4.27±0.07	5
0.640	4.20	30.2 ±1.0	4.72±0.16	5
0.912	-	24.6 ±0.3	2.70±0.03	3
1.54	-	43.4 ±0.3	2.81±0.02	4
		50°C		
0.0101	-	10.1 ±0.1	100 ± 1	4
0.0101	4.83	7.21±0.17	71.4 ±1.7	5
0.0202	-	7.88±0.63	39.0 ±3.1	4
0.0299	-	9.13±0.35	30.5 ±1.2	4
0.0597	-	9.77±0.37	16.4 ±0.6	4
0.149	-	13.7 ±0.3	9.19±0.20	4
0.275	-	18.3 ±0.5	6.66±0.20	4
0.279	3.70	34.9 ±1.2	12.5 ±0.4	5
0.284	4.54	32.5 ±0.6	11.4 ±0.2	4
0.299	0.700	21.9 ±0.1	7.32±0.01	2
0.299	1.66	24.9 ±0.6	8.34±0.19	4
0.307	-	20.5 ±0.4	6.66±0.12	4
0.307	3.70	30.1 ±0.3	9.80±0.07	4
0.307	4.54	33.1 ±0.9	10.8 ±0.03	4

Table 1 (continued)

1	2	3	4	5
0.455	-	27.4±0.4	6.03±0.09	5
0.767		38.5±0.7	5.03±0.09	4
		Additions of $NaClO_4$		
		50°C		
0.322	1.00	21.1±0.4	6.55±0.10	4
0.322	4.00	25.1±0.3	7.80±0.09	4
0.322	5.29	27.5±1.0	8.54±0.32	4

[redacted] Number of measurements at the NaOH and salt concentration considered.

[redacted] Wavelength λ = 260 nm was used.

[redacted] Wavelength λ = 320 nm was used.

Discussion

The dependence of the second order rate constants (k_{II}) on $\sqrt{\mu}$ (μ - ionic strength) (Fig.2) found in this work completely differs from analogous relationships usually observed in the case of the reaction between ions of the same sign. If we assume similarly to the alkaline hydrolysis of alkyl salicylates that in the o-OH-phenyl benzoate alkaline hydrolyse reaction both acidic and anionic forms are involved, we could write:

$$AH + OH^- \underset{k_1}{\overset{K}{\rightleftharpoons}} A^- + H_2O \qquad (6)$$

$$AH + OH^- \xrightarrow{k_1} X \qquad (7)$$

$$A^- + OH^- \xrightarrow{k_2} X \qquad (8)$$

$$K = \frac{[A^-]}{[AH][OH^-]}$$

AH and A^- denote the acidic and anionic forms of o-OH-phenyl benzoate.

Proceeding from the total rate equation

$$v = (k_1 [AH] + k_2 [A^-]) [OH^-]$$

the effective pseudomolecular rate constant k_I could be expressed as follows:

$$k_I = \left(\frac{k_1}{1 + K [OH^-]} + \frac{k_2 K [OH^-]}{1 + K [OH^-]} \right) [OH^-] \qquad (9)$$

$$k_I.const = k_1/K + k_2 \left[OH^-\right] \qquad (10)$$

$$const = \frac{1 + K \left[OH^-\right]}{K \left[OH^-\right]} \qquad (11)$$

$$K = \frac{K_a}{K_W}$$

K_W is the ionic product of water.

Equations (5) and (10) could be considered as analogical: terms in the right sides are identical but the left side of Eq. (10) differs by the term "const".

In the case of both Eqs. (5) and (10) the second order rate constant for the anionic form k_2 could be equalled with the slope of the relationship between the effective pseudo-first order rate constants k_I or k_I.const values and the alkali concentration. The values of the second order rate constants for the acidic form could be found from the corresponding intercepts.

It should be noted that the applicability of Eqs. (10) and (5) does not necessarily mean that the acidic and anionic forms are involved according to the above reaction scheme. So, for instance, Eqs.(10) and (5) may embrace also such cases when together with the acidic form the ion pairs are involved:

$$AH + OH^- + K^+ \overset{K}{\rightleftharpoons} A^- + K^+ + H_2O \overset{K_{ass}^{-1}}{\rightleftharpoons} A^- K^+ \qquad (12)$$

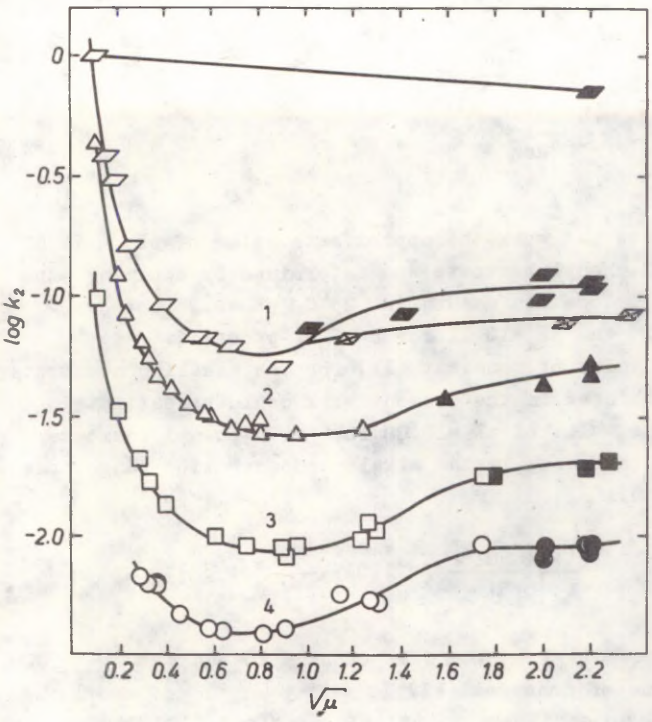


Fig. 2. Dependence of the effective values of k_{II} for the alkaline hydrolysis of o-OH-phenyl benzoate on $\sqrt{\mu}$.
1. 50°C (▱); 2. 40°C (△);
3. 25°C (□); 4. 15°C (○).
Shaded points - with additions of NaCl;
▨ - with additions of $NaClO_4$

$$AH + OH^- \xrightarrow{k_1} X \qquad (13)$$

$$A^- K^+ \quad OH^- \xrightarrow{k_2} X \qquad (14)$$

$$K^1 = K \,.\, K_{ass}^{-1} \qquad (15)$$

In the present work the approximate value of pK_a = 10.08 for o-OH-phenyl benzoate was determined by applying the spectrophotometric method (at 25°C pK_a=9.45 for pyrocatechol[8] and pK_a=10.11 for o-OC_2H_5-phenol[8]).

The value of constant (11) for the alkali concentration range embraced in the present work could be estimated using the value of pK_a=10.08 for o-OH-phenyl benzoate.

For instance, in the alkali concentration range from 0.01 to 0.1

$$\frac{1 + K\,[OH^-]}{K\,[OH^-]} = 1.01 \;\div\; 1.001$$

Consequently, in the case of $pK_a \ll 10$ and at $C_{OH^-} > 0.01$ the value of constant (11) is very near to one and Eqs. (5) and (10) appear to be identical. Constant (11) differs more from one in the case of $pK_a > 10$ and at $C_{OH} < 0.01$. Under such conditions the assumption $\xi \ll a-x$ applied to derive Eq. (5) is evidently not valid.

Consequently, when treating the data of o-OH-phenyl benzoate alkaline hydrolysis ($C_{OH^-} \gg 0.01$) by Eq. (10), constant(11) does not practically differ from one. Therefore, the values of the second order rate constants k_2 were found from the first linear part of the relationships between the effective pseudo- first order rate constants k_I and the alkali concentration (Fig.3). The values of the second order rate constants for the corresponding acidic form k_1 were calculated from the intercepts of the plots k_I versus

C_{OH^-} (see Eq.10).

The obtained second order rate constants of o-OH-phenyl benzoate alkaline hydrolysis for the anionic form k_2 and for the acidic form k_1 at 15, 25, 40 and 50°C are listed in Table 2. It presents also the hydroxide concentration ranges embraced at the determination of k_2 and k_1 values.

For the purpose of comparison the values of k_2 and k_1 calculated from the k_I constants in Table 1 by Eq. (10) for the compound for which pK_a=11.0 (i.e. in Eq.(10) const ≠ 1) are given in Table as well.

The relationships between the second order rate constants k_{II} and $\sqrt{\mu}$ (see Fig.2) are also in accordance with the conclusion that the o-OH-phenyl alkaline hydrolysis involves both the acidic and the anionic form or the ion pairs of the anionic form, the rate constants of which differ about 10^3 times. A relatively low alkali concentration brings about a decrease in the rate constants k_{II}, however, at a higher alkali concentration (or ionic strength) an increase in the alkali concentration (or ionic strength) is accompanised by a new rise of the k_{II} constants. This shows that at the lowest alkali concentrations mainly the OH- form is involved. A higher alkali concentration increases the relative rate of the reaction which involves the anionic form or ion pairs of the latter. At the highest alkali concentrations (or ionic strength) the k_{II} constant goes up again and a positive salt effect can be observed.

Using the value pK_a=10.08 for o-OH-phenyl benzoate and the alkaline hydrolysis rate constants for both the anionic form or ion pairs of anionic form, k_2, and the acidic form, k_1, the ratio of the reaction rates of the above forms at various alkali concentrations could be estimated . For instance, at 25°C, C_{OH^-} = 0.1, v_{AH}/v_{A^-} or $v_{AH}/v_{A^-K^+}$ =1.43 and at C_{OH^-} =1 $v_{AH}/v_{A^-(A\text{-}K^+)}$ = 0.143.

Table 2

Parameters of Correlation Equations

$$k_I = k_1/K + k_2 [OH^-] \quad (5)$$

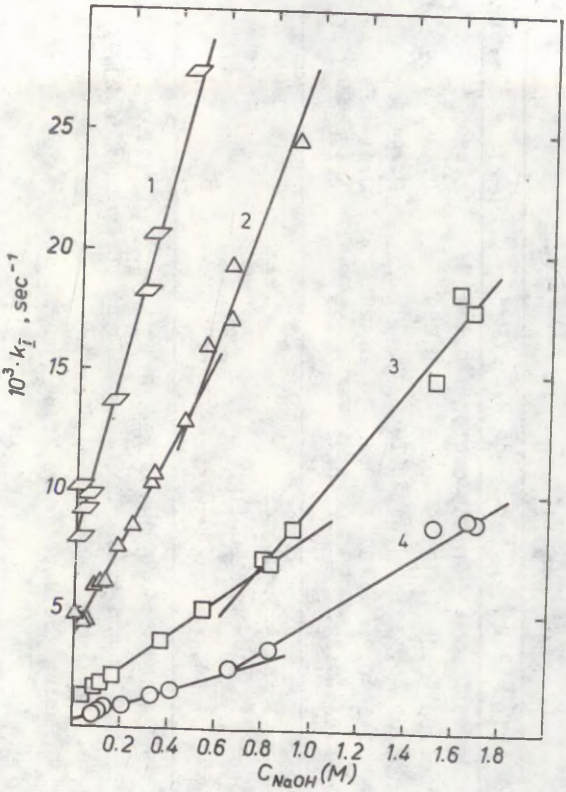
$$k_I.const = k_1/K + k_2 [OH^-] \quad (10)$$

Temperature °C	$10^3.k_1/K=k_1'$	$10^3 . k_2$ ($M^{-1}.sec^{-1}$)	Range of alkali concentrations	n/n_o**	r	s	Equation***
15	0.325±0.018	3.21±0.08	$(8.25\text{-}41.2).10^{-2}$	21/22	0.987	0.060	(5)
	0.352±0.023*	3.15±0.10*	$(8.25\text{-}41.2).10^{-2}$	21/22	0.987	0.060	(10)
25	1.05 ±0.15	7.25±0.07	$(3.94\text{-}54.5).10^{-2}$	23/23	0.999	0.063	(5)
	1.08 ±0.16	7.22±0.07*	$(3.94\text{-}54.5).10^{-2}$	23/23	0.999	0.064	(10)
40	3.69 ±0.07	21.1±0.4	$(1.09\text{-}45.5).10^{-2}$	41/49	0.993	0.329	(5)
	3.75 ±0.07*	21.0±0.4*	$(1.09\text{-}45.5).10^{-2}$	41/49	0.993	0.324	(10)
50	7.29 ±0.10	43.3±0.7	$(2.02\text{-}30.7).10^{-2}$	17/24	0.994	0.283	(5)
	7.35 ±0.17*	42.8±1.2*	$(2.02\text{-}30.7).10^{-2}$	17/24	0.992	0.606	(10)

* The value of $pK_a = 11.0$ was used (const ≠ 1).

** n/n_o – Denominator reflects the total number of data, involved in regression data processing and numerator equals the number of the remaining points after excluding significantly deviating points.

*** The number of equation by which the data treatment was carried out.



Fiq. 3. Dependence of the effective k_I values on the alkali concentration.

1. 50°C (▱)
2. 40°C (△)
3. 25°C (□)
4. 15°C (○)

Table 3

Values of k_1, k_{salt}, $\Delta \log k_{salt} = \log k_{salt} - \log k_2$ and Activation Parameters E and logA for Alkaline Hydrolysis of o-OH-Phenyl Benzoate

Temperature °C	k_1*	$10^2 \cdot k_{salt}$**		$\Delta \log k_{salt}$	
		$\sqrt{\mu} = 2.2$	$\sqrt{\mu} = 2.0$ and 2.2	$\sqrt{\mu} = 2.2$	$\sqrt{\mu} = 2.0$ and 2.2
15	4.24 ***	0.901±0.008	0.865±0.015	0.448	0.430
25	8.65; $2.07 \cdot 10^2$	1.99 ±0.05	1.99 ±0.05	0.439	0.439
40	16.68	5.02 ±0.13	4.66 ±0.10	0.377	0.344
50	23.19	11.1 ±0.2	11.2 ±0.4	0.429	0.414
		8.54 ±0.32****	8.17±0.21****	0.295****	0.276****

$E_1 = 8.994 \pm 0.613$ kcal/mole $\log A_1 = 7.49 \pm 0.44$

$E_2 = 13.837 \pm 0.151$ kcal/mole $\log A_2 = 8.01 \pm 0.11$

$E_{salt} = 13.243 \pm 0.334$ kcal/mole $\log A_{salt} = 7.99 \pm 0.24$

* $k_1 = \dfrac{k_1' \cdot K_a}{K_w}$ At 15,25,40 and 50°C the values of K_w $4.51 \cdot 10^{-5}$, $1.01 \cdot 10^{-14}$, $2.92 \cdot 10^{-14}$ and $5.47 \cdot 10^{-14}$ as well as pK_a values 10.23, 10.08, 9.88 and 9.76 were used. The latter were found from the pK_a value 10.08 at 25°C, using the dependence of pK_a on the temperature of phenol[8].

** $\mu = C_{NaCl(NaClO_4)} + C_{NaOH}$.

*** In calculations[4] for o-OH-phenyl benzoate the pK_a value 8.70 found in borate buffer[13], was used.

**** As a neutral electrolyte $NaClO_4$ was used.

Despite the fact that at the alkali concentration 0.1 M more than 99% of the reagent studied is in the anionic form, in the total reaction rate the reaction involving the acidic form still dominates.

At low alkali concentrations the additions of NaCl almost do not influence the rate of reaction. The positive salt effect is observed only at the highest concentrations of alkali, or, if to the relatively concentrated alkali solution ($C_{OH^-} > 0.25$). NaCl or $NaClO_4$ is added (see Fig.2). The values of salt effects in the presence of $NaClO_4$ are about 0.1 log units less than those observed in the presence of NaCl.

The values of rate constants k_{salt} characteristic of the high electrolyte concentrations in the presence of NaCl and $NaClO_4$ as well as the values of salt effects

$$\triangle \log k_{salt} = \log k_{salt} - \log k_2$$

are listed in Table 3. It presents also the values of the activation parameters E and logA, calculated from the k_1, k_2 and k_{salt} values respectively.

When discussing the data obtained a question arises whether the k_2 constants correspond to the alkaline hydrolysis of the o-OH-phenyl benzoate anionic form or to the ion pairs of the anionic form.

If we consider that the k_2 constants belong to the alkaline hydrolysis of the o-OH-phenyl benzoate anionic form, then at the alkali concentration $0.4 < C_{OH^-} < 1$ $\log k_{II} - \log k_2 \approx$ ≈ 0.10 i.e. in the reaction mainly the anionic form of o-OH-phenyl benzoate is involved. It should be noted that when studying previously the salt effects of the reactions involving substrates with a charged substituent, the substrate was found in the state of ion pairs at the electrolyte concentrations considered. Besides, it should be noted that the salt effects in the presence of NaCl and $NaClO_4$ were found too small for the anionic form, and their values almost coincide with the specific salt effects calcu-

lated by equation[9]:

$$\triangle \log k^{x}_{salt} = a \lg k^{x}_{o} + b$$

where x denotes the substituent and $\log k_o$ belongs to the zero concentration of the electrolyte added.

At 50°C in the presence of NaCl additions ($\sqrt{\mu}$ =2.2) one can write:

$$\triangle \log k^{calc}_{salt} = -0.30 \log k_2 - 0.060 = -0.30(-1.364) - 0.060 = 0.349$$

and in the presence of the $NaClO_4$ additions ($\sqrt{\mu}$ = 2.3)[9]:

$$\triangle \log k^{calc}_{salt} = -0.57(-1.364) - 0.44 = 0.337$$

For the o-OH-phenyl benzoate anionic form the following total salt effect could be expected in the presence of NaCl[10,11]

$$\triangle \log k^{calc}_{salt} = \triangle \log k_{el} + \triangle \log k_{sp} = 1.07 + 0.349 = 1.42$$

which is considerably higher than it was observed in the present work.

Taking into account the above-mentioned fact it is more likely that the k_2 constant belongs to the alkaline hydrolysis of the o-OH-phenyl benzoate ion pairs and at the alkali concentrations $0.4 < C_{OH^-} < 1$ o-OH-phenyl benzoate is almost totally in the state of ion pairs. At the higher concentrations of the electrolyte the specific salt effect of ion pairs is observed. It is evidenced also by the conductometric data of o-OH-phenyl tosylate in the alkaline solution[2], according to which it could be considered that o-OH-phenyl tosylate is present as ion pairs already at the relatively low concentrations of alkali.

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KINETICS OF THE REACTION OF TETRAETHOXYSILANE WITH ETHYLMAGNESIUM CHLORIDE IN ETHYL ETHER AND IN THE MIXTURES OF ETHER WITH TOLUENE

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The kinetics of the interaction of tetraethoxysilane with ethylmagnesium chloride was investigated by means of a thermographic method. The rate constants of consecutive steps of the reaction diminish with gradual substitution of ethoxy groups for ethyl ones in the silane. The reaction of ethyltriethoxysilane was investigated in detail as a model one. The pseudo-first order rate constants depend linearly on the concentration of tetrameres calculated for the solution of ethylmagnesium chloride. The additions of toluene markedly increase the reaction rate. In the presence of the reaction product, ethoxymagnesium chloride, the reaction rate increases slightly.

I General Kinetic Characteristics of the Process

The alkylalkoxysilanes have gained great importance in industry. Unlike the alkylhalosilanes, they hydrolyze more slowly and so the formation of its polymers can be easily controlled.

One of the most important methods of obtaining substituted ethers of orthosilicon acid is based on the interaction of organomagnesium compounds with tetraalkoxysilanes. This reaction was discovered long ago[1] and is being successfully used in laboratory scale and in industry[2-4]. Never-

theless, the kinetic features of the reaction have not been investigated. However, the detailed kinetic characteristics of the process are needed urgently to control the latter in order to obtain the mixtures of monomers of set composition.

The interaction of tetraalkoxysilanes with organomagnesium compounds (in this case tetraethoxysilane with ethylmagnesium chloride) consists in the following sequence of reactions:

$$Si(OEt)_4 + EtMgCl \xrightarrow{k_1} EtSi(OEt)_3 + EtOMgCl \quad (1)$$

$$EtSi(OEt)_3 + EtMgCl \xrightarrow{k_2} Et_2Si(OEt)_2 + EtOMgCl \quad (2)$$

$$Et_2Si(OEt)_2 + EtMgCl \xrightarrow{k_3} Et_3SiOEt + EtOMgCl \quad (3)$$

$$Et_3SiOEt + EtMgCl \xrightarrow{k_4} Et_4Si + EtOMgCl \quad (4)$$

The presence of four consecutive steps considerably complicates the total kinetics of the process. The data about the possibility to accomplish the last step (4) are contradictory. However, no doubt it proceeds very slowly. The attempts to obtain tetraalkylsilanes by means of this reaction have usually not been successful[2,4]. It is thought widely[5,3] that alkyltrialkoxysilanes react with alkylmagnesium halides at a higher rate than the tetraalkoxysilanes, i.e. $k_2 > k_1$.

The kinetics of the reaction was followed thermographically, by heat evolution during the process . The measurements were carried out in pseudofirst order conditions with a great excess of ethylmagnesium chloride to exclude the influence of reaction products on the kinetics. The effect of ethoxymagnesium chloride on the reaction rate was investigated by means of some special experiments. As reaction media ethyl ether and its mixtures with toluene were used. Although in practical applications nonetheral media are preferred, to obtain reliable kinetic features of the process, we had to carry out the investigation in homogeneous media that was achieved by using a solvent able to

solvate ethylmagnesium chloride. The kinetic measurements were accompanied with determination of the composition of the reaction mixture by means of GLC after reaction (heat evolution) was completed.

Thermographic investigation of the reactions of tetraethoxysilane and ethyltriethoxysilane under the conditions mentioned above yielded the same rate constants within the range of experimental error. The reaction mixtures after the accomplishment of heat evolution contained in both cases almost only diethyldiethoxysilane. Triethylethoxysilane could be detected in reaction mixtures, decomposed in several hours after the reaction of tetraethoxy- or ethyltriethoxysilane had ceased.

One can observe a temperature jump at the beginning of the processe on the thermograms of the reaction of tetraethoxysilane (Fig.6). It indicates that there proceeds a fast reaction with heat evolution. Consequently, the rate of the reaction of tetraethoxysilane considerably exceeds that of the reaction of ethyltriethoxysilane and the former reaction does practically not influence the heat evolution during the kinetic measurements. The reaction of diethyldiethoxysilane is essentially slower* and therefore also can not be investigated by means of our thermographic method. Hence, a sequence $k_1 > k_2 > k_3 > k_4$ is established.

Further we investigated the kinetics of the reaction of ethyltriethoxysilane with ethylmagnesium chloride in detail assuming that the found features are valid also for the reactions of all alkylalkoxysilanes. The dependence of k_2 on the concentrations of ethylmagnesium chloride, added toluene, and ethoxymagnesium chloride was investigated. The standard deviation of k_2 for a separate kinetic curve was about 9% of relative value.

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* according to our estimation $k_3 \lesssim 10^{-3}$ sec $^{-1}$ at 30°C in 1,2 M solution of ethylmagnesium chloride in ethyl ether.

2. Kinetics of Ethyltriethoxysilane in Ethyl Ether

The reaction of ethyltriethoxysilane with ethylmagnesium chloride (2) was investigated as a model reaction for alkylalkoxysilanes. The pseudo-first order reaction rate constants were determined for various concentrations of ethylmagnesium chloride. Their values are given in Table 1. The dependence of rate constants on the concentration of Grignard reagent is represented in Fig. 2.

Table 1.

Pseudo-first order rate constants for the reaction of ethyltriethoxysilane (initial conc. 0.048 M) with ethylmagnesium chloride in ethyl ether at 30°C

EtMgCl (M)	k (sec^{-1})
0.90	0.014 ± 0.0011
1.09	0.016 ± 0.0012
1.45	0.035 ± 0.0034
2.03	0.040 ± 0.0036
2.16	0.054 ± 0.0051
2.32	0.063 ± 0.0060
3.22	0.088 ± 0.0086

It is seen from Fig. 1. that the formal reaction order for ethylmagnesium chloride exceeds the unit. Our attempts to determine the order of the reaction from the dependence in coordinates lg k — lg [EtMgCl] revealed that the reaction order slightly depends on the concentration of the Grignard reagent but has a mean value about 1.5. This may indicate a complicated mechanism of the reaction, but it is most likely that it may be connected with changes in the nature of the grignard reagent when its concentration is altered. It is known[6] that organomagnesium compounds are

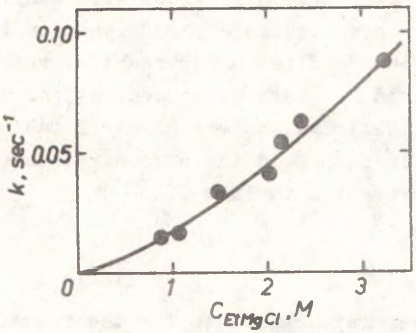
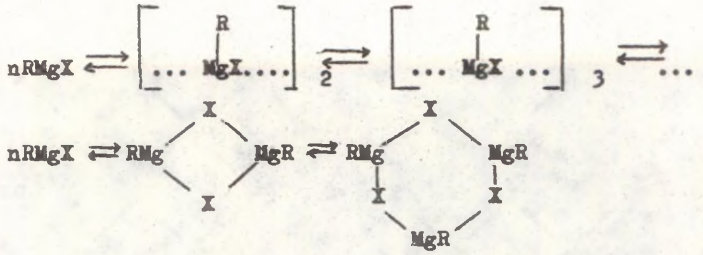


Fig. 1. Dependence of the pseudo-first order rate constant of the reaction of ethyltriethoxysilane on the concentration of ethylmagnesium chloride in ethyl ether at 30°C.

highly associated, moreover, the degree of association increases with an increase in the concentration of the solution. On that bases one can assume that the increase in reaction rate is in this case connected with higher reactivity of associates. In order to verify this assumption we made an attempt to estimate the composition of the solution of ethylmagnesium chloride at various concentrations.

The paper by Walker and Ashby[6] gives the dependence of apparent degree of association of ethylmagnesium chloride on its molal concentration in ethyl ether. Already at low concentrations the degree of association is close to a value equal to 2. By increasing the concentration of the solution the degree of association increases and approaches 3. This indicates low content of monomers even at moderate concentrations and the predominance of dimers and higher associates at any concentration.

The same authors put forward the linear or cyclic association of the Grignard reagent:



It is necessary to pay attention to the fact that independently of the degree of association in both schemes any magnesium atom is solvated by one molecule of ether. Such a model of the association does not permit to connect an increase in the degree of association with a decrease in the concentration (activity) of ether in the solution. On the other hand, it is known[7], that in the absence of solvating solvents organomagnesium compounds are highly polymerized.

In our opinion it is reasonable to assume, particularly for ethylmagnesium chloride, the following association equilibria:

$$2M \cdot 2Et_2O \overset{K_1}{\rightleftharpoons} D \cdot 2Et_2O + 2Et_2O \qquad (5)$$

$$2D \cdot 2Et_2O \overset{K_2}{\rightleftharpoons} T \cdot 2Et_2O + 2Et_2O \qquad (6)$$

where M, D and T denote monomers, dimers and tetramers respectively. The possible structures of these particles are represented in Fig. 2.

The assumption of formation of tetramers of structure C (in Fig.2) enables us to explain i) an increase in association when the content of ether in the solution drops, ii) relatively high solubility of the reagent in hydrocarbons (e.g. in toluene) owing to nonpolar alkyl groups on the surfice of the molecule, iii) increased reactivity of higher associates, as will be discussed further.

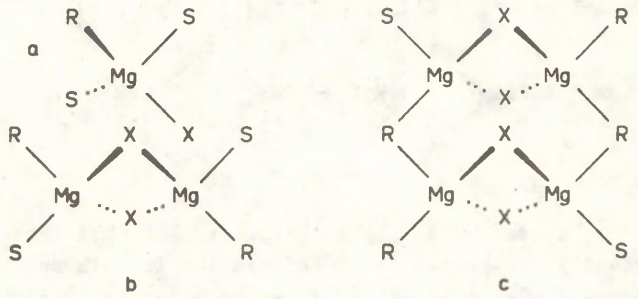


Fig. 2. Assumed structures of disolvated monomers (a), dimers (b) and tetramers (c) of ethylmagnesium chloride. For the sake of simplicity the two-center and three--center bonds are represented equally.

We applied the experimental data of Walker and Ashby[6] to estimate the content of various particles in the solution of ethylmagnesium chloride. To convert these data into the molarity scale we have determined experimentally the dependence of the density of ethylmagnesium chloride etheral solution on its concentration (see Exp. part). Then, neglecting the low content of monomers at high concentration of the solution and assuming the values of association equilibrium constant, K_2 (eq.6), we calculated the dependence of the association degree on concentration. The best agreement of the calculated curve with the experimental one was obtained at $K_2 = 175 \pm 25$ mole.l^{-1} . Further it is not difficult to obtain monomer, dimer and tetramer concentrations for any titrated concentration of ethylmagnesium chloride (Table 2).

On the bases of these data one can also estimate the value of K_1 (eq.5) about $1,5 \times 10^4 \div 2 \times 10^4$ mole.l^{-1} . It was assumed similarly to the paper by Walker and Ashby[6] that each magnesium atom was solvated by one molecule of ether. Realizing that these data are rather approximate, we nevertheless assume that they characterize at least qualitatively the state of ethylmagnesium chloride in ethyl ether.

Plotting of our kinetic data against the data of the composition of the solution of ethylmagnesium chloride revealed a proportionality between the rate constant and the concentration of tetramers in solution (Fig.3) with a slope

$$k_{tetramer} = 0.13 \pm 0.02 \ l \cdot mole^{-1} \cdot sec^{-1}.$$

Table 2

Composition of solution of ethylmagnesium chloride in ethyl ether

Molar concentrations of				
titrated solution	monomer	dimer	tetramer	free ether
0.1	0.015	0.04	0.003	9.4
0.5	0.021	0.15	0.047	8.9
1.0	0.004	0.23	0.135	8.2
1.5	...	0.28	0.24	7.5
2.0	...	0.30	0.35	6.6
2.5	...	0.31	0.47	5.9
3.0	...	0.29	0.60	5.1

Some more complicated reaction schemes were considered quantitatively, e.g. involving the reaction i) only dimers, ii) dimers with the displacement of ether, iii) dimers and tetramers with the displacement of ether, iiii) competitively dimers with the displacement and tetramers without displacement of ether. None of these schemes led to reasonable results. Moreover, latter variant directly indicated

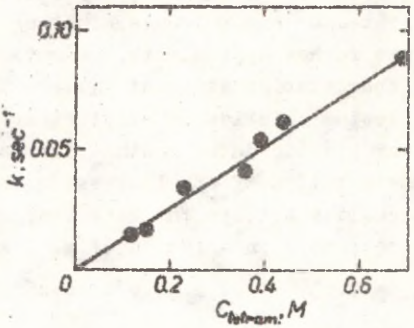


Fig. 3. Dependence of the rate constant of the reaction of ethyltriethoxysilane with ethylmagnesium chloride on the concentration of tetramers in the solution

the participation of only tetramers in the reaction without the displacement of ether.

Such a result agrees well with our assumption about the structure of tetramers (Fig. 2.,c). Apparently, the transition state of the reaction is either cyclic

or the reaction starts with an attack of the ethoxyl group on the magnesium atom. In both cases the most advantageous (most electrophilic) center of the reaction must be at the magnesium atom bound to alkyl groups. Monomers and dimers do not contain such magnesium atoms. The influence of the bridging alkyl group (evidently that of a donor group), which decreases the electrophilicity of magnesium atom, must be somewhat weaker than the analogous effect of ether ligand since the alkyl bridges appear only when the concentration

of solvating ether drops. The examination of molecular models revealed less steric hindrances at this center in comparision with the magnesium atom bound to ether. It is known[5] that the reaction is highly susceptible to steric hindrances in a organomagnesium compound. Hence, ether exerts an unfavourable effect on the reaction because of blockading the active centers of the reagent.

3. Kinetics in Mixtures of Ether with Toluene.

Synthesis of alkylalkoxysilanes is frequently carried out in nonetheral media (in aromatic hydrocarbons)[2-4]. To obtain some information about the effect of nonsolvating solvent we investigated the reaction of ethyltriethoxysilane with ethylmagnesium chloride in mixtures of ether with toluene. The obtained pseudo-first order rate constants are presented in Table 3. Because of the high degree of association of the Grignard reagent the molar ratio of toluene in the mixtures is calculated on the bases of an assumption that each molecule of ethylmagnesium chloride is solvated by one molecule of ether. The dependence of a reaction rate constant on the content of toluene in the mixture is represented in Fig. 4.

Table 3

Pseudo-first order rate constants of the reaction of ethyltriethoxysilane (initial conc. 0.024 M) with ethylmagnesium chloride (conc. 0.89-0.92 M) in mixtures of ethyl ether with toluene at 30°C

Molar ratio of toluene	k, sec^{-1}
0	0.014 ± 0.0011
0.26	0.017 ± 0.0017
0.50	0.058 ± 0.0056
0.69	0.131 ± 0.0112
0.80	0.167 ± 0.0150

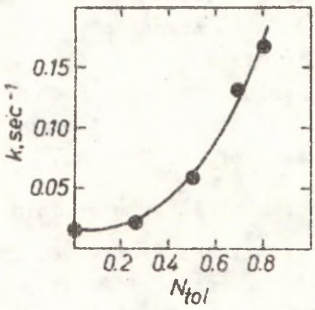


Fig.4. Dependence of the rate constant of the reaction of ethyltriethoxysilane with ethylmagnesium chloride on molar ratio of toluene in etheral solutions.

It can be seen from these data that the additions of toluene markedly accelerate the reaction. Such an influence of toluene could be predicted since a decrease in ether content in solution violates the association equilibrium towards the formation of reactive tetramers (see the above parts). However, the total effect of toluene additions can not be explained by a displacement of association equilibrium for even in the case when all ethylmagnesium chloride is tetrameric, the rate constant under the given conditions (conc. ethylmagnesium chloride 0.9 M) can not exceed 0.12 sec $^{-1}$ ($K_{tetram.}$ = 0.13 l.mole^{-1}). Consequently, the additions of toluene exert also some accelerating influence on the reaction. The observed effect can not be explained by medium polarity alternation for the Grignard solutions have very high dielectric susceptibilities[8] and replacement of a considerable part of ether for toluene practically does not influence the effective polarity of the solution. It is likely that toluene, and probably other aromatic solvents as well, interact specifically with the transition state of the reaction reducing its energy. Such a conclusion is acceptable in connection with high polarizability of these compounds.

4. Influence of Products on Reaction Kinetics

The kinetic experiments described in the previous parts of this work were carried out under pseudo-first order conditions with a great excess of ethylmagnesium chloride to exclude the influence of reaction products. When applying the reaction to preparative purposes there is no excess of the reagent and then alkoxymagnesium halide accumulating during the reaction (see eq. 1-4) exerts a certain influence on the kinetics of the process. Thus, for instance, halogenomagnesium alkoholates formed during the reaction markedly suppress the rate of the Grignard reaction with ketones[9,10].

To determine the influence of ethoxymagnesium chloride on the reaction rate, we investigated the kinetics of the reaction between ethyltriethoxysilane and ethylmagnesium chloride with various amounts of ethoxymagnesium chloride present in the reaction mixture. A great exess of the Grignard reagent in relation to silane was used. Variation of the molar ratio EtMgCl/EtOMgCl was achieved by adding certain amounts of absolute ethanol to samples of the Grignard reagent so that the concentration of ethylmagnesium chloride was the same in all the experiments (about 1 M). After the violent reaction had ceased the reagents were used for kinetic measurements, The obtained pseudo-first order rate constants are given in Table 4.

It appears that in the presence of the reaction product, ethoxymagnesium chloride, the rate slightly increases. One can assume that ethoxymagnesium chloride causes an increased association of ethylmagnesium chloride for it is known that in the presence of oxygen compounds the degree of association of the Grignard reagent increases[11]. On the bases of the ideas developed in Part 2 the structures of tetrameric complexes of ethylmagnesium chloride with ethoxymagnesium chloride in Fig. 5 may be taken for granted.

Table 4

Pseudo-first order rate constants of the reaction of ethyltriethoxysilane (initial conc. 0.024 M) with ethylmagnesium chloride (conc. about 1 M) in the presence of various amounts of ethoxymagnesium chloride

EtOMgCl/EtMgCl	k . sek $^{-1}$
0	0.018 ± 0.0016
0.30	0.024 ± 0.0021
0.50	0.030 ± 0.0027
0.73	0.031 ± 0.0030
0.98	0.034 ± 0.0032
1.26	0.035 ± 0.0030

The value of the rate constant for the complex (a) in Fig. 5 must be about two times less than that for an ordinary tetramer of ethylmagnesium chloride (because of the statistical factor). Reactivity of the complex (b) is not likely to exceed the reactivity of dimers, i.e. the complex is practically not involved in the reaction. The same enables us to explain a slight influence of little additions of ethoxymagnesium chloride on the reaction rate and the decrease of the effect by the gradual increase of the additions (see Table 4). One can also predict a decrease of the accelerating effect of ethoxymagnesium chloride at low and high concentrations of ethylmagnesium chloride, and the absence of the positive effect of alkylmagnesium chloride in the cases when tetramers of alkylmagnesium halides do not take part in the reaction.

5. Experimental Section

Reagents and Solvents

Ethyl Ether was purified from peroxides with potassium hydroxide, dried over heated calcium chloride and distilled over sodium.

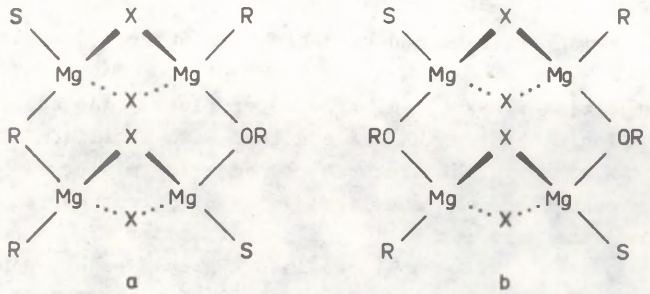


Fig. 5. The assumed structures of tetrameric complexes of ethylmagnesium chloride with ethoxymagnesium chloride. For the sake of simplicity the two-center and three-center bonds are not distinguished.

Toluene was treated with conc. sulfuric acid, dried over calcium chloride and, before use, distilled over sodium wire.

Ethylmagnesium Chloride was prepared as usual[12] from ethyl chloride ('medical' grade) and metallic magnesium in the dry ethyl ether, avoiding the access of air moisture. Before use the Grignard reagent solutions were diluted with ethyl ether or toluene and the solution concentrations in basic magnesium were determined by titration.

Ethyl Alcohol was dried at first with calcium oxide and after that with magnesium ethylate.

Tetraethoxysilane, $n_D^{20} = 1.3837$; $d_4^{20} = 0.9670$

Ethyltriethoxysilane, $n_D^{20} = 1.3854$; $d_4^{20} = 0.9232$

Kinetic Measurements

The thermographic method used has been described earlier[13,14].

The reaction flask (35-ml Erlenmeyer flask) was capped with a teflon stopper which was equipped with a silicon rubber disk. Through the disk was placed a thermistor MT-54 which was connected into a bridge-system of direct current. The thermograms were recorded by a potentiometer EZ-8.

The reaction flask was placed into a glass vessel, whose temperature was kept at $30\pm0.1^{\circ}C$ by means of a thermostat U-10. The reaction mixture was stirred by a magnetic stirring bar.

Before the kinetic runs 20 ml of the Grignard reagent solution was placed into the reaction flask. After reaching the system of a constant temperature ($30^{\circ}C$), 0.1-0.2 ml of corresponding silane was introduced through the silicon rubber disk by a hypodermic syringe and the thermograms were recorded. The examples of thermograms are presented in Fig. 6.

The thermograms were transferred into kinetical curves by numerical integration from the plot of ΔT vst in accordance with the formula[14]

$$\Delta T_o = \Delta T + \rho \int_0^t \Delta T(t)dt,$$

where ΔT is the temperature difference between the reaction flask and the thermostat at any time t; ΔT_o is the integral temperature difference ; ρ is the cooling coefficient.

The coefficient ρ was determined experimentally as follows. After the silane had reacted to completion, 0.02-0.05 ml of acetone was added to the reaction mixture. A very fast exethermic reaction proceeded and the corresponding cooling curve was recorded.

The value of the coefficient ρ was calculated from the equation

$$\rho = \frac{1}{t_2 - t_1} \ln \frac{\Delta T_1}{\Delta T_2} \quad .$$

The first order rate constants were calculated by the differential method[15] from kinetical curves. In accordance with this method the first order rate constant is equal to the slope (with an opposite sign) in the plot of $\ln \Delta\Delta T / \Delta t$ vs τ, where t is the time; ΔT is the temperature gradient of the reaction mixture at any time t; τ is the time corresponding to the intermediate of the time interval Δt.

The standard deviation of a single value of the rate constant averages 9% of the relative value.

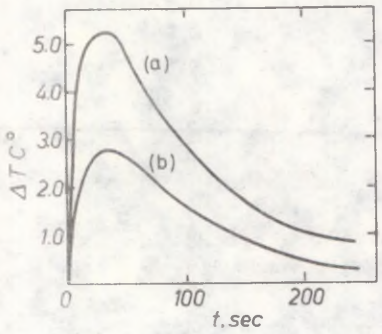


Fig.6. Examples of thermograms for the reaction of tetraethoxysilane (a) and ethyltriethoxysilane (b) with ethylmagnesium schloride (~1.2.M) in ethyl ether.

Analysis of Reaction Products

After the heat liberation had ceased the reaction mixture was with precaution poured into the cold water. The organic layer was separated, dried over anhydrous magnesium sulfate and analyzed by the GLC method.

The analysis was done on a ЛХМ-8МД chromatograph with a catarometer: the metallic column (4mm x 2 m) was filled

with polydimethylsiloxane on Chromaton-N-Super 0.125 ÷ 0.160 mm. The gas-carrier was helium, the temperature of the column being 80°C.

Determination of density of ethylmagnesium chloride.

The density of ethylmagnesium chloride ethereal solutions was determined at 30°C by picknometer of 25 ml. The results are reported in Table 5.

Table 5.

Density of Ethylmagnesium Chloride in Ethyl Ether at 30°C

EtMgCl	d_4^{30}
0	0.714
1.08	0.773
2.40	0.851
3.05	0.864
4.44	0.949

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC DATA IN THE GAS PHASE HOMOLYSIS. 2. Results of Data Treatment in the Coordinates of the Isokinetic Relationship.

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The results of the statistical treatment of available kinetic data for the gas phase homolytic dissociation in the coordinates log k_{T_2} - log k_{T_1} have been presented. The results of the treatment according to the Arrhenius equation of the parallel independent data sets for separate reactions are listed as well.

The slope of the linear dependence between log k_{T_2} and log k_{T_1} is indistinguishable from the value of the ratio T_1/T_2. Formally, this corresponds to a special case of isoentropic behavior. In fact, this proves the absence of the linear dependence between log A and E. Also it proves the existence of the effective mean value log A_o = 14.64 for the complete data set. The log A_o values for special subsets are somewhat variable. For the fission of the aliphatic nitro compounds the log A_o value is equal to 16 and significantly differs from the general mean value cited above.

One can interpret the obtained results as the mutual independence of structural effects influencing on the log A and E. Besides, the

dependence of log k on the structure is mainly determined by the corresponding changes in E values.

The reaction of the unimolecular gas phase homolytic dissociation:

$$R_i - R_j \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_i^{\cdot} + R_j^{\cdot} \qquad (1)$$

is the source of free radicals and plays an important role in the theoretical analysis of mechanisms and prediction of the results for the gas phase homolytic thermal reactions. The determination of the experimental rate constants for the indicated reaction is highly complicated and the reliability of the obtained results remains generally unsatisfactory. Therefore the respective possible theoretical calculation methods deserve to be studied. General and reliable enough calculation methods for the rate constant estimation of the gas phase homolytic dissociation are lacking in literature. Quantum chemical approaches to solve this problem remain out of the framework of reports of this series. There have been attempts to derive the corresponding empirical relations. So, Tsang (see ref. 1) starting from the data for the reactions

$$AA \underset{k_r(AA)}{\overset{k_f(AA)}{\rightleftharpoons}} 2\,A. \qquad (2)$$

$$BB \underset{k_r(BB)}{\overset{k_f(BB)}{\rightleftharpoons}} 2\,B. \qquad (3)$$

(symbols used by the author are retained) proposes equations (4) and (5) for the estimation of the frequency factor ν_{AB} and the activation energy E_{AB} of the reaction (1) (i.e. $A\text{-}B \rightleftarrows A^{\cdot} + B^{\cdot}$) :

$$\nu_{AB} = \left[\frac{k_r^2(AB)}{k_r(AA)k_r(BB)} \right]^{1/2} (\nu_{AA}\ \nu_{BB})^{1/2} \exp \frac{S_{AA}+S_{BB}-S_{AB}}{2\ R} \qquad (4)$$

$$E_{AB} = 1/2\ (H_{AA} + H_{BB} - 2H_{AB}) + 1/2(E_{AA} + E_{BB}) \qquad (5)$$

Equation (5) follows automatically if one proposes that E_{AB} value is the difference between the sum of the free radicals A° and B° formation enthalpies and the formation enthalpy of the compound AB. Analogous considerations must be kept for the fission reactions of AA and BB. This idea seems to be natural and fruitful and we shall use it in a somewhat more concrete manner in the following reports of this series.

As for the estimation of the ν_{AB} value according to Equation (4), the known values of the recombination rate constants of the free radicals which form not only AA and BB but also AB, are necessary. Besides, the entropy values of all dissociating compounds are needed. Therefore, independently of the degree of the adequacy of Equation (4), the above approach can't serve in this form as the basis for a general calculation scheme. As in the case of any other reaction class one can represent the rate constants of unimolecular gas phase homolytic dissociation as the straightforward function from the corresponding dissociation free energies. From the point of view of the transition state theory these values are defined by the independent contributions determined by activation enthalpy and entropy. Unfortunately, up to now no successful independent quantitative calculations of the indicated values for any kind of the representative reaction class have been carried out.

Within the framework of the formal approach, for reaction series where only one influential factor is variable, one can often describe observed experimental data in the

coordinates of the isokinetic dependence. The latter assumes linearity between the entropy and enthalpy of activation or an equivalent linear relationship between the logarithm of the preexponential factor log A and the activation energy E (for a review of the corresponding literature see ref. 2). Besides, the isoentropic ($\Delta S_{\neq}$ or log A = const.) and the isoenthalpic ($\Delta H_{\neq}$ or E = const.) reaction series may be considered to be the special cases of the isokinetic dependence as well. It is of certain interest to check the isokinetic dependence for the gas phase homolysis reactions. In the present case from the very beginning one can hardly distinguish any single variable factor which could allow us to include all the reactions of type (1) into single isokinetic series. Consequently, the treatment of the whole data set or even subsets which correspond to the constant breaking bond appears to be rather an arbitrary procedure. Therefore, one must be particularly careful when interpreting the results obtained. If there exists no dependence between the values log A and E of the treated data set, the result may correspond formally either to the isoentropic or isoenthalpic special case. The former is to take place if the observed lg k dependence on the structure of the dissociating compound is mainly caused by the corresponding changes in E values. Less significant changes in the log k values, independent of E, and caused by the variance of log A values simulate then random deviations within the framework of the data treatment scheme used.

Similarly formal isoenthalpic behavior could be observed if the changes in log A values are of fundamental importance and the variance of E values occurs like a result of random and comparably moderate deviations.

The question of the preexponential factor of the gas phase unimolecular reactions has been discussed in many reports (see for example ref. 3-6 and the literature cited in them). Within the framework of the transition state theory $A = (ekT/h) \exp(\Delta S_{\neq}/R)$.

The conception of loose and tight activated states is discussed[5]. For the first ones $\Delta S_{\neq} > 0$ and log A > 13. For the latter ones $\Delta S_{\neq} < 0$ and log A < 13. The forming free radicals obtain rather additional degrees of freedom. Therefore the assumption of the loose activated state for gas phase homolysis seems to be more natural. The majority of log A values observed support this assumption. It is noted that for the decomposition and isomerization reactions in 75 cases out of one hundred lg A≈12 ÷ 15, i.e. the average is 13.5. In the review[6] the log A values for 800 unimolecular gas phase reactions are divided into three groups. 47% of them have log A = 12 - 14, in 33% cases log A > 14 and in 20% reactions log A < 12. Several attempts of the theoretical estimation of the ratio of the partition functions for activated and initial states of the gas phase unimolecular reactions in the region of high pressures could be cited[5-7]. However, these estimations are practically impossible if some arbitrary, in fact, additional assumptions are not introduced. Those ones deal with the degree of the change of the stretching and torsional vibration frequencies when the transition state is formed. Therefore, it is understandable, why this approach doesn't result in general quantitative relationships adequate enough to serve as the foundation of the calculation scheme which could really be applied to the computational estimation of rate constants.

The activation parameters used in the present paper are mainly extracted from the tables of V.I. Vedeneev and A.A. Kibkalo[8]. Besides, the data from more recent publications were used. A complete compilation of these data will be listed in the next paper of this series. Only the high pressure and falloff limit data were used.

A remarkable uncertainty is accompanied with the activation parameters of reaction (1) reported in the literature. One can hardly find out any criteria of general application (the analysis of experimental methods used or some kind of preliminar treatment of data) the use of which ones may be successfully applied for the preliminar selection

of more reliable data.

Technique of Data Treatment.

The available kinetic data were processed in coordinates of the linear relationship between $\log k_{T_2}$ and $\log k_{T_1}$ related to two different temperatures $T_2 \neq T_1$:

$$\log k_{T_2} = a + \varkappa \log k_{T_1}, \qquad (6)$$

where

$$\varkappa = (T_2 - \beta)T_1 / (T_1 - \beta)T_2, \qquad (7)$$

$$a = \log A_o(1 - \varkappa), \qquad (8)$$

β is the isokinetic temperature.

In the special isoentropic case $\beta = \pm \infty$ and $\varkappa = T_1/T_2$. In the isoenthalpic case $\beta = 0$ and $\varkappa = 1$.

The value A_o of the expression (8) has the meaning of the preexponential factor if $E = 0$. In the special isoentropic case A does not depend on the considered reaction and it is numerically equal to A_o. Usually only activation parameters of the homolytic dissociation have been listed in the majority of literature sources. Therefore one cannot directly use the experimental values of $\log k_{T_1}$ and $\log k_{T_2}$. Besides, experimental data of different reactions belong to different temperature ranges. Consequently, total data processing for all homolytic dissociation reactions using experimentally measured values of k_{T_1} and k_{T_2} is not realizable. Therefore, the extrapolated or interpolated to temperatures T_1 and T_2 log k values calculated from reported in the literature values of log A and E for corresponding reactions were used. Although the activation parameters are sometimes in rough errors the log k values calculated from log A and E are more reliable. In the case of interpolation this reverse calculation of

log k values leads to uncertainties, comparable with experimental errors. Moving away from the basic temperature range studied the uncertainty of extrapolations are increasing, of course. The temperatures $T_1 = 700^{\circ}$ and $T_2 = 800^{\circ}K$ were selected as the average values of the corresponding under and upper limits of experimental temperatures using all independent estimates of activation parameters.

We attempted to determine presumably more reliable averaged Arrhenius parameters using simultaneously all different independent data for a single reaction. For every independent pair of log A and E values corresponding log k_T were calculated at three temperatures T_{min}, T_{max} and T_{mean}. The last ones equal to under, upper and mean values of temperature ranges studied experimentally. These log k_T values for every reaction represented by more than one independent data source were treated in the coordinates of the Arrhenius equation:

$$\log k_T = \log A - E(1/2.3RT) \qquad (9)$$

The statistical corrections were introduced when more than one equivalent breaking bond was present in the substrate undergoing the homolysis.

The data treatment was performed by means of a computer Nairi-2 using a program for linear regression analysis with the automatic exclusion of points according to Student's criteria on the confidence levels 0.99 and 0.95.

Results and Discussion .

Table 1 lists the results of the data treatment in the coordinates of Equation (9) for the reactions for which parallel independent literature values of log A and E are available. Altogether, the data sets for forty-four reactions were processed. At the beginning of the treatment the number of points is equal to the three-fold number of independent log A and E pairs available. Generally small values of standard deviations s indicate a statistical compatibility of the data sets used. The calculated log A and E values are

within the limits of the variation of the log A and E values used or close to these limits. Poorly consistent data sets result in the calculated values of log A and E which differ considerably from these reported in corresponding original sources. (see for example reactions for $C_2H_5Hg-C_2H_5$, $CH_2=CHCH_2-CH_2CH=CH_2$, etc.). In this case the procedure of calculations according Equation (9) does not make sense.

We have to mention also the essential differences in temperature ranges the available data cover. It is natural that the data based on wider temperature ranges studied lead to more reliable values of activation parameters.

As for concrete estimates of log A values for different reactions, the observed variance of them is no doubt significant. At the same time it is hard to give any simple interpretation of the observed changes in log A values when the structure of the dissociating compound is varying.

A linear relationship between the literature values log A and E is not observed. The same is true for the activation parameters obtained as a result of the simultaneous treatment of the different independent data in the coordinates of Equation (9).

The results of the statistical treatment of data in the coordinates of Equation (6) are listed in Table 2. The data sets selected according to the constancy of the breaking bond and the total set comprising all the available data were processed. At first let us examine the results obtained for the latter set (see also Fig. 1).

Altogether 365 independent pairs of log k_{700^oK} and log k_{800^oK} estimates were comprised. In the course of the treatment fifteen points were excluded according to the Student criterion, however the numerical a and α values of Equation (6) were practically not affected. The value $\alpha = 0.877 \pm 0.002$ is indistinguishable from the ratio T_1/T_2 even on the confidence level equalling 0.99. Consequently, the whole data set is formally described as an isoentropic series and unimolecular gas phase homolytic

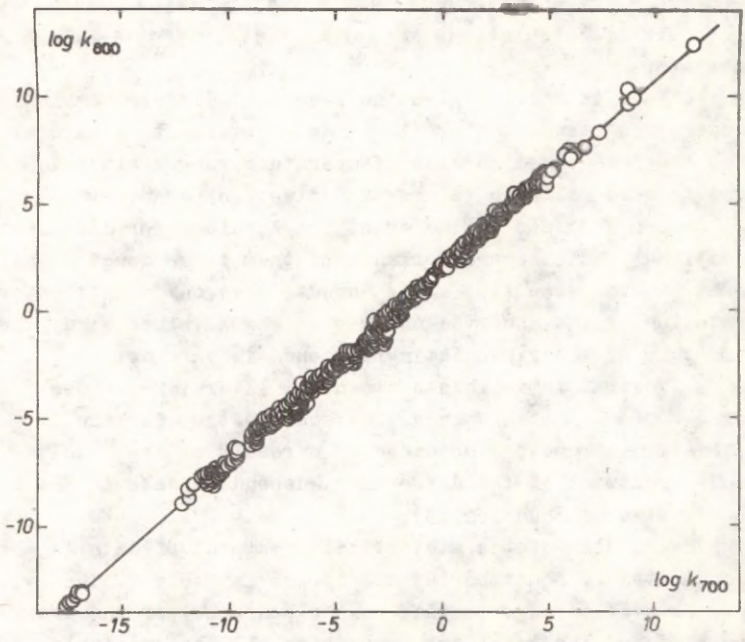

Fig. 1. Dependence in coordinates of Equation (6) comprising the total data set of all the breaking bond types.

dissociation is characterized by mean (effective) value of the preexponential factor $\log A_o = 14.64 \pm 0.04$*.

The linear dependence in the coordinates of Equation (6) covers the ranges of $\log k_{T_1}$ and $\log k_{T_2}$ changes nearly thirty logarithmic units. In this connection even relatively large errors of these values can not distort noticeably the resulting dependence.

In the case of separate subsets of data the conclusions are less certain as the large relative significance of large experimental errors is much higher. Nevertheless, the data of Table 2 indicate that almost in all the cases α and T_1/T_2 values are more or less indistinguishable, i.e. separate subseries also satisfy the isoentropic criterion. So one can neglect all generally little enough differences between α and T_1/T_2 values and conclude that all the special series also correspond to the formally isoentropic case. Another question is the real constancy of the indicated universal value of $\log A_o$. The results obtained from limited data sets for the majority subseries can hardly solve this problem. There are only three sufficiently representative (more than thirty points) subseries and characterized by the high precision the isoentropic version of the isokinetic relationship is followed. These series correspond to the rupture of bonds C-C, C-NO_2 of aliphatic nitro compounds and O-O of peroxides (see Table 2.) For the first and the latter of these subseries the special effective $\log A_o$ values equalling 15.03 ± 0.30 and 14.67 ± 0.57, respectively, are indistinguishable from the universal effective value. The second series is characterized by the $\log A_o = 15.99 \pm 0.13$ which is already distinguishable from the universal value 14.64 ± 0.04.

In the remaining cases $\log A_o$ values of the special series are hardly reliable.

The results of the similar treatment of $\log k_{T_1}$ and $\log k_{T_2}$ values, calculated according to the data of Table 1,

* Here and further standard deviations are indicated.

are given at the end of Table 2. One can see that after the exclusion of five points from fifty-three α values for three different pairs of T_1 and T_2 are indistinguishable from T_1/T_2, and log A_o differs little from the general effective value. Log A_o becomes fully indistinguishable from this averaged value after the exclusion of nine points.

The results presented above show that the observed variation of log A values could not be described within the framework of the isokinetic dependence. To consider the gas phase unimolecular homolysis as a truly isoentropic reaction series can hardly be justified, too. It follows from Equation (6) that random true deviations Δ in log k values make a contribution equalling $\Delta_{mean}(1-\alpha)$, to the value s where Δ_{mean} is the square-root mean value of Δ. From the values s = 0.21 for T_1 = 700 and T_2 = 800°K and s = 0.7 for T_1 = 600 and T_2 = 1000°K (see Table 2) it follows that corresponding Δ_{mean} values are 1.68 and 1.75, respectively. The compatibility of these values shows that the observed error-corridors for the dependences in the coordinates log k_{T_2} and log k_{T_1} are determined rather by the real variability of log A values than only by random errors in experimental log k values.

Assuming that $\Delta_{mean} \approx 1.7$ one can conclude that 2/3 of all log A values are placed in the range from 13.0 to 16.5, and 95% in the range from 11.2 to 18. Generally it corresponds to the situation observed for the total set of original data.

So, the results of the statistical treatment confirm that the main influence of structural effects on log k values for gas phase homolysis is realized as a result of the corresponding changes in E values. At the same time the variation of log A values makes an essentially smaller contribution.

One can estimate also the upper limit of a standard error SMX due to the use of the universal effective mean log A_o value instead of true individual values for every considered reaction:

$$SMX = 2.3RT\ \Delta_{mean} \cdot 10^{3}\ \text{kcal/mole}$$

According to this formula the value ≈ 6 kcal/mole for 750°K is obtained. Consequently, the observed degree of adequacy, when using the calculation scheme founded on the neglection of the real variation of the log A value, may be almost wholly due to this circumstance. If the standard deviation for the description of data within the framework of such a calculation scheme is essentially lower than the cited estimate of SMX one can interpret this result as a sign of essentially more restricted variability of log A when compared with the above estimation proceeding from the s value of the linear regression in the coordinates of Equation (6). As far as the experimental errors in log k values were ignored in the course of the SMX value estimation, namely this is the result to be expected.

The data for substituted nitro benzene fission reactions forming NO_2 free radical need a special discussion. The isokinetic dependence with $\beta \approx 837°K$ has been reported earlier[9]. Later new data were published[10] but they have little to do with the data of ref. 9. From these data follows also the validity of linearity in the coordinates of Equation (6) while $\alpha = 0.838 \pm 0.014$ differs significantly from $T_1/T_2 = 0.911$ (see Table 2). The indicated α value leads to the isokinetic temperature $\beta = 1525°K$. The same order value follows from the approximate linearity between E and log A values listed in paper[10]. The value $\log A_o = 7.24 \pm 0.17$ is apparently not an universal log A value for all the compounds of the discussed series.

This example of linear dependence between E and log A corresponds to the reaction series with a clearly identified variable factor - the substituents in the aromatic cycle. Nevertheless we cannot firmly believe in the reality of this result, because there remain doubts on the degree of the reliability of rate constants from Ref. 10. The data from

different independent sources for unsubstituted nitro benzene are available for comparison. In paper[10] the used values log A = 17.3±0.3 and E = 69.7±1.4 kcal/mole correspond to log $k_{688}{}^{o}{}_{K}$ = -4.84. Besides, the values log A = =12.65 and E = 53.4 kcal/mole (log $k_{688}{}^{o}{}_{K}$ = -4.32) have been published[9]. In a recent paper[11] the values log A = = 15.7±1.3 and E = 67.3±4.4 kcal/mole (log $k_{688}{}^{o}{}_{K}$ = -5.68) have been reported.

The fact of the linear dependence in the coordinates of Equation (6) could not prove the reliability of the used log k values. This is clearly illustrated by the means of data reported in Ref.9.

Taking into account these considerations one must additionally analyze the data of paper[10] before a definite conclusion may be drawn about the character of this reaction series.

The results obtained in the present study do not exclude a possibility that the real isokinetic relationship is hold for other suitably choosen sets of data. In this connection it could be noted that for the discussed data for substituted nitro benzenes the conclusion about the significant difference between α and T_1/T_2 values corresponds to the variation of log A values in relatively narrow limits from 16.7 to 17.5 (only one compound has log A= = 16.0).

Table 1

Results of the Data Treatment in the Coordinates of the Arrhenius Equation (9) for Reactions Represented by Independent Parallel Literature Data.

ΔT - general temperature range ^{o}K
s - standard deviation, kcal/mole
n - total number of points

The second line for any reaction corresponds to the result after the exclusion of significantly deviating points according to the Student's criterion on the confidence level 0.95.

No	Reaction	ΔT	log A	E, kcal/mole	s	n	Ranges of literature values	
							log A	E, kcal/mole
1	2	3	4	5	6	7	8	9
1.	$CH_3 - H$	995 - 1800	14.3 ± 0.5	99.3 ± 3.0	0.37	15	14.1-16.5	101.0-107.6
2.	$4\text{-}CH_3\text{-}C_6H_4CH_2\text{-}H$	795 - 1373	14.7 ± 0.2	80.5 ± 1.1	0.11	9	13.7-14.4	76.0- 79.5
		-"-	14.6 ± 0.2	80.3 ± 0.8	0.08	8	-"-	-"-
3.	$CH_3\text{-}CH_3$	748 - 1418	15.1 ± 0.6	82.8 ± 2.5	0.42	27	14.5-17.5	79.3- 91.7
		748 - 1057	17.4 ± 0.3	91.7 ± 1.2	0.12	21	-"-	-"-
4.	$(CH_3)_2CH\text{-}CH_3$	300 - 853	17.9 ± 0.5	80.1 ± 1.3	0.73	12	17.8-18.9	80.0- 83.1
5.	$(CH_3)_3C\text{-}CH_3$	713 - 1240	17.4 ± 0.2	83.4 ± 0.8	0.13	21	16.1-18.1	77.8- 85.6
6.	$CH_2{=}CHCH_2\text{-}CH_3$	689 - 1046	12.5 ± 1.4	60.4 ± 5.7	0.65	12	12.7-16.3	59.1- 71.5
		-"-	12.4 ± 0.5	58.5 ± 1.9	0.21	9	-"-	-"-

Table 1 continued

1	2	3	4	5	6	7	8	9
7.	$C_6H_5CH_2-CH_3$	823-1010	14.5±0.9	69.1±3.6	0.16	9	13.0-14.7	63.2-70.1
8.	$4-CH_3-C_6H_4-CH_3$	795-1373	14.4±1.2	79.0±5.3	0.55	9	12.3-14.7	67.0-81.8
9.	CH_3CO-CH_3	600-1101	12.5±1.0	60.2±4.5	0.72	12	14.1-15.4	68.0-72.0
10.	C_2H_5-I	660-800	12.7±1.0	46.8±3.4	0.20	9	11.9-14.3	45.0-51.6
		-"-	14.1±0.8	51.2±2.5	0.13	7	-"-	-"-
11.	NH_2-NH_2	933-1600	15.3±0.8	68.8±4.4	0.62	15	11.7-13.0	48.0-60.0
		-"-	15.6±0.5	72.1±2.7	0.37	12	-"-	-"-
12.	$C_6H_5CH_2-NH_2$	829-1250	12.9±0.4	59.7±1.7	0.13	9	12.8-15.2	59.0-71.9
		-"-	13.0±0.2	60.0±0.8	0.06	8	-"-	-"-
13.	CH_3-NO_2	583-1500	15.5±0.8	56.3±2.4	0.63	21	11.4-16.3	42.8-58.5
14.	$CH_3N=N-CH_3$	463-1300	16.0±0.5	51.5±1.6	0.52	21	14.0-17.0	46.0-53.0
		502-1300	17.4±0.1	54.7±0.3	0.09	11	14.5-17.0	49.6-53.0
15.	$CF_3N=N-CF_3$	572-760	15.3±0.3	53.1±0.9	0.08	12	14.0-16.2	48.5-55.2
16.	CH_3O-NO	463-1000	13.8±0.1	37.5±0.2	0.07	9	12.9-13.3	34.0-36.4
17.	C_2H_5O-NO	435-513	17.3±1.2	44.6±2.5	0.18	11	13.2-14.1	34.7-37.7
18.	C_3H_7O-NO	443-503	16.4±0.8	41.8±1.9	0.10	9	13.2-14.4	34.7-37.6
19.	$C_2H_5O-NO_2$	370-800	22.1±4.6	50.4±10.0	2.54	12	14.7-20.7	38.0-41.2
		434-488	11.8±1.9	31.4±4.0	0.21	9	14.7-16.8	-"-
20.	$C_2H_5O-OC_2H_5$	403-518	11.1±2.3	26.8±4.6	0.69	15	12.0-16.1	29.9-37.3
		407-518	13.4±0.4	32.1±0.8	0.09	9	12.7-16.1	30.4-37.3

Table 1 continued

1	2	3	4	5	6	7	8	9
21.	$(CH_3)_3CO-OC(CH_3)_3$	363-623	15.6±0.3	37.4±0.5	0.19	36	13.3-16.6	34.0-39.1
		-"-	15.8±0.1	37.6±0.2	0.08	30	15.6-16.6	37.4-39.1
22.	CH_3Hg-CH_3	563-881	13.5±0.8	51.1±2.7	0.51	21	13.1-15.7	50.1-58.0
		567-881	11.4±0.3	43.7±0.9	0.14	14	13.1-15.0	-"-
23.	$C_2H_5Hg-C_2H_5$	590-690	23.2±12.2	71.9±35.2	1.88	9	13.0-15.4	42.5-49.5
24.	CH_3Cd-CH_3	742-844	10.6±2.4	40.0±8.6	0.29	9	11.9-13.4	45.8-48.8
25.	N_2-O	1400-2500	10.0±0.5	54.7±4.1	0.39	21	8.9-11.4	48.2-59.5
		1500-2200	9.2±0.1	49.7±1.1	0.08	13	8.9-10.1	48.2-55.0
26.	$C_6H_5CH_2-C_2H_5$	860-1036	14.0±0.8	64.5±3.5	0.13	6	12.5-14.9	57.5-68.6
27.	$CH_2=CHCH_2-CH_2CH=CH_2$	866-1070	26.7±4.5	109.7±20.0	0.78	6	13.3-13.4	45.6-56.0
28.	CF_3-CF_3	1325-1873	19.9±0.9	108.5±6.7	0.25	6	17.6-18.2	94.4
29.	$C_6H_5CH_2-C_3H_7$	863-1008	14.1±2.3	64.5±9.6	0.30	6	14.47-14.5	65.0-67.2
30.	NF_2-NF_2	351-680	14.8±0.1	18.8±0.2	0.06	6	15.0-15.4	19.4-19.8
31.	$C_6H_5CH_2-NHCH_3$	819-1187	13.3±0.4	59.5±1.6	0.11	6	12.9-15.1	57.7-68.7
32.	Cl_3C-NO_2	411-443	15.4±1.7	37.3±3.3	0.12	6	15.3-15.7	37.4-37.7
33.	$C(NO_2)_3-NO_2$	359-596	17.3±0.2	40.3±0.4	0.08	6	16.3-17.6	38.6-40.9
34.	$(CH_3)_2CHN=N-CH(CH_3)_2$	503-673	13.67±0.03	40.7±0.1	0.005	6	13.68-13.76	40.75-40.9
35.	$(CH_3)_3CN=N-C(CH_3)_3$	453-559	20.9 ±1.7	52.3±3.8	0.28	6	16.3-17.1	42.8-43.0
36.	$(CH_3)_2CHO-NO$	443-500	13.9±0.2	36.6±0.4	0.02	6	14.1-14.4	37.0-37.6
37.	C_4H_9-NO	475-512	17.0±4.9	43.3±11.1	0.27	6	13.6-14.5	36.2-37.0
		475-500	23.0±4.0	56.7±9.1	0.18	5	-"-	-"-

Table 1 continued

1	2	3	4	5	6	7	8	9
38.	CH_3O-OCH_3	393-453	12.3±1.6	30.0±3.1	0.18	6	15.2-15.6	35.3-36.9
39.	$(CH_3)_2CHO-OCH(CH_3)_2$	373-458	15.8±0.3	38.0±0.5	0.04	6	15.1-15.4	36.8-37.1
40.	CH_3O-CH_3	750-936	11.0±3.2	59.1±11.9	0.55	6	15.0-17.5	76.0-81.0
41.	$C_2H_5Pb-C_2H_5$	506-548	10.6±4.1	32.8±9.8	0.29	6	12.1-12.6	36.9-37.0
42.	$(CH_3)_3Si-Si(CH_3)_3$	770-1020	25.6±1.5	111.9±6.0	0.40	9	12.2-17.2	49.5-80.5
43.	$(CH_3)_2NH=N-N(CH_3)_2$	398-539	15.9±1.5	39.5±3.0	0.43	9	11.4-14.4	31.9-36.1
44.	$FO-NO_2$	363-403	15.3±0.7	33.1±1.2	0.06	6	15.0-15.4	31.8-32.3

Table 2

Results of the Data Treatment in the Coordinates of Equation (6)

n - number of points

r - correlation coefficient

s - standard deviation, kcal/mole

Significantly deviating points were excluded according to the Student's criterion on the confidence level 0.99

Breaking bond	T_1	T_2	T_1/T_2	α	a	n	r	s	log A_o
1	2	3	4	5	6	7	8	9	10
C - H	1057	1212	0.872	0.869 ± 0.025	1.744 ± 0.095	20	0.9923	0.22	13.64 ± 0.74
				0.838 ± 0.012	1.584 ± 0.048	19	0.9981	0.10	12.39 ± 0.38
C - C	900	1025	0.878	0.857 ± 0.13	1.832 ± 0.036	80	0.9900	0.21	15.03 ± 0.30
C - Cl	808	890	0.908	0.985 ± 0.033	1.656 ± 0.115	5	0.9983	0.15	17.97 ± 1.25
C - Br	879	987	0.891	0.886 ± 0.004	1.435 ± 0.006	15	0.9999	0.02	13.12 ± 0.06
C - I	732	851	0.860	0.858 ± 0.031	1.983 ± 0.047	8	0.9961	0.10	14.18 ± 0.34
N - N	781	1037	0.753	0.806 ± 0.010	3.198 ± 0.005	10	0.9993	0.16	12.95 ± 0.022
C - N	703	820	0.857	0.895 ± 0.015	2.066 ± 0.038	9	0.9990	0.15	14.48 ± 0.27
C - NO_2	533	609	0.875	0.895 ± 0.007	1.995 ± 0.019	40	0.9987	0.14	15.99 ± 0.15
(aliphatic)				0.890 ± 0.006	1.995 ± 0.016	39	0.9991	0.12	15.99 ± 0.13

Table 2 continued

1	2	3	4	5	6	7	8	9	10
C - NO_2* (aromatic)	688	755	0.911	0.838±0.014	1.171±0.069	15	0.9982	0.02	7.24±0.17
C-NN-C	561	659	0.851	0.865±0.022	2.364±0.076	23	0.9927	0.19	15.90±0.51
O - O	422	493	0.056	0.859±0.025	2.159±0.092	33	0.9870	0.20	14.99±0.64
				0.842±0.022	2.112±0.081	32	0.9893	0.18	14.67±0.57
O - NO	494	536	0.922	1.015±0.034	1.297±0.082	14	0.9930	0.04	16.55±1.06
O - NO_2	435	528	0.824	0.976±0.030	3.353±0.093	6	0.9982	0.17	19.04±0.53
				0.904±0.081	3.047±0.332	5	0.9881	0.17	17.30±1.89
C - O	772	884	0.873	0.879±0.036	1.928±0.19	7	0.9957	0.17	15.22±1.50
C - S	773	886	0.873	0.889±0.012	1.820±0.025	9	0.9993	0.07	14.28±0.20
C - Hg	673	768	0.876	0.863±0.020	1.631±0.058	14	0.9967	0.17	13.19±0.48
The total set	700	800	0.875	0.880±0.002	1.815±0.006	365	0.9986	0.25	14.52±0.05
				0.877±0.002	1.830±0.005	350	0.9991	0.21	14.64±0.044
The data from Table 1	700	800	0.875	0.894±0.008	1.93±0.02	53	0.9975	0.44	15.44±0.16
				0.885±0.002	1.81±0.02	48	0.9984	0.29	14.48±0.16
				0.881±0.005	1.84±0.01	42	0.9991	0.22	14.72±0.68

* Data of ref. 10. The fission reaction of 4-nitro aniline is not taken into account since the very large deviation for the corresponding point

Table 2 continued

1	2	3	4	5	6	7	8	9	10
	637	961	0.663	0.703±0.022	5.24±0.08	53	0.9753	1.19	15.54±0.24
				0.663±0.017	4.80±0.07	48	0.9842	0.78	14.24±0.21
				0.668±0.014	4.94±0.05	42	0.9910	0.59	14.65±0.15
	600	1000	0.600	0.640±0.025	6.24±0.12	53	0.9624	1.42	15.60±0.30
				0.597±0.019	5.69±0.10	48	0.9759	0.93	14.23±0.25
				0.604±0.016	5.86±0.08	42	0.9862	0.70	14.65±0.20

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